Appendix B

Laboratory Standard Operating Procedures

SOP No. AP-CM-5	Revision: 15	Effective: 08 OCT 10	Supercedes: 02 SEP 10
POLYCHLORINATED DIBENZO DIOXIN/FURANS **USEPA METHODs 8290, 1613, 23, 0023A & TO-9A**			
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This version contains at the end of this document, a summary of the enhanced features or modifications to the reference method and describes any changes or clarifications where the reference method is ambiguous or provides insufficient details. It also embodies information acquired over 29 years of experience in PCDD/Fs analyses.

1. PURPOSE/IDENTIFICATION
    1. **This procedure describes the analytical techniques used for extraction and analysis of aqueous, solid, oil, wipe, waste, air and tissue samples for polychlorinated dibenzo dioxins and furans (PCDD/PCDF) by EPA Methods 8290, 1613, 23, 0023A, &TO-9A.**
2. APPLICABLE MATRICES
    1. This method is applicable to all matrices. .
3. DETECTION LIMIT
    1. The limits of detection and quantitation in various matrices are available in the Performance Commitment document.
4. SCOPE AND APPLICATION
    1. This method is intended to apply to all PCDD/F extractions performed at Analytical Perspectives, regardless of matrix. It is consistent with the Final Rule on the Methods Innovation Rule 40 CFR Parts 63, 268, et al.; June 14 th, 2005; pp. 34538-34592.
5. SUMMARY OF THE TEST METHOD
    1. For solid samples, the percent solids is determined. The samples are conditioned appropriately, depending on matrix. The samples are fortified with extraction standards and then extracted by a number of means, depending on which is appropriate for the matrix in question. Following extraction, additional conditioning may be necessary, after which the sample extracts are concentrated and fortified with additional standards for clean-up. A variety of clean-up procedures, usually including gravity-fed column chromatography with acid and base impregnated silica are employed. Extracts are then concentrated, fortified with injection standards, and undergo final preparations for HRGC/HRMS. The extracts are analyzed by HRGC/HRMS.
6. DEFINITIONS
    1. Definitions (and more thorough explanations) of concepts introduced by Analytical Perspectives may be found in the Performance Commitment document.
7. INTERFERENCES
    1. Several classes of compounds can interfere with the quantification of PCDD/Fs. Most notable are polychlorinated diphenyl ethers (PCDPEs), which can appear as false PCDF peaks. Polyaromatic hydrocarbons can also present significant interference at high concentrations.
8. SAFETY
    1. Standard sample preparation laboratory safety precautions apply, as outlined in AP's Health and Safety SOPs.
9. EQUIPMENT AND SUPPLIES
    1. Autosampler
    2. DEC Alpha Station with Opus Quan Data System or PC with MassLynx.
    3. Neslab Water Coolers.
    4. MM Autospec Magnetic Sector High-Resolution Mass Spectrometer.
    5. Pipet, disposable, serological, 10mL.
    6. Amber glass bottles, 1 L (Teflon-lined screw cap).
    7. Two –L separatory funnels.
    8. Teflon boiling chips.
    9. glass chromatographic columns
        1. Place a glass wool plug at the bottom of the column, pack with 1g of silica gel, 4 g NaOH/silica gel, 1 g of silica gel, 8 g of H 2SO 4/silica gel, 2 g silica gel, 1 g Na 2SO 4.
    10. N-Evaporator.
    11. Conical vials, 2mL.
    12. Glass fiber filters and glass wool plugs.
    13. Funnels, 100 mL.

14. Dean-Stark Trap, condenser and flask.
15. Rotary Evaporator.
16. Round bottom flasks, 500mL.
17. Top-Loader Balance.
18. Oven.

10. REAGENTS, STANDARDS AND SOLVENTS

1. Reagents
    1. Sulfuric acid, concentrated.
    2. Silica gel. Highest purity grade.
    3. Celite 545.
    4. Water, distilled.
    5. Florisil.
    6. Prepurified nitrogen gas.
    7. Anhydrous sodium sulfate.
    8. Sodium Hydroxide. Highest available purity.
2. Solvents
    1. Methylene chloride. Highest available purity.
    2. Hexane. Highest available purity.
    3. Tetradecane. Highest available purity.
    4. Acetone. Highest available purity.
    5. Methanol. Highest available purity.
3. Standards
    1. Analytical standards (Cambridge Isotope Laboratory, Wooburn, MA).

11. COLLECTION, PRESERVATION, AND HANDLING

1. Amber glass bottles and jars must be used for collection.
2. Fish tissue is stored at -20 ° C, all other samples are stored at 4 ° C, extracted within 30 days and completely analyzed within 45 days of extraction

12. QUALITY CONTROL

1. Method Blank (MB): Method blank is a sand, Hydromatrix TM, Na 2SO 4 or distilled water preparation that is free of native analytes that has been prepared and analyzed using the same procedures followed for the rest of the analytical batch. For air samples, the MB is resin or PUF prepared from the same batch used for the field samples. The MB is kept in house at 4 0 C until the field samples are returned.
    1. A method blank is run with every analytical batch or 20 samples (whichever is less) per matrix type.
    2. All samples within an analytical batch are re-extracted and analyzed if the method blank associated with that batch does not meet the criteria described above.
2. On-Going Precision & Accuracy (OPR = LCS): Applicable only to true 1613 assays. This redundant sample is prepared by adding a known quantity of native standards to a matrix and is supposedly used to assess method performance (precision and accuracy). One OPR is analyzed per matrix.
    1. A known amount of native PCDD/Fs is used for spiking.
    2. The OPR of each native isomer should have a relative percent difference as per Method 1613, which defines the tolerance windows that must be met.
    3. Extraction standard recoveries should range between Method 1613's tolerances.
    4. If the Extraction Standard recovery of an isomer in the OPR and the associated sample(s) is also out of the range, the sample and the OPR will be re-extracted and analyzed.
    5. It is AP's policy to develop a database of sample projects where both the OPR and the BCS3 are analyzed for M1613 samples. Once the Laboratory Director has determined that such information has been obtained, then, any project completed under M1613 where an OPR is required will NOT have a BCS3. Only those projects not requiring an OPR will be processed and analyzed under the BCS3 system. Furthermore, when an OPR is required, only a CS3 – spiked with the usual isomeric interferences and the first and last eluters – will be analyzed at the beginning of the sequence. No ending CS3 will be done when OPR is required.
3. Matrix Spike (MS/MSD): Prepared by adding a known quantity of native standards to a sample matrix before the extraction. These are normally done upon request and are considered as billable.

1. A known amount of native PCDD/Fs is used for spiking.

2. The relative percent difference between MS/MSD samples should be ±20 percent provided the matrix used does not contain PCDD/Fs at levels impairing the measurements. Limits are based on the variances that are typically allowed with the methods' relative response factors.

4. Duplicate Samples: Duplicate samples are two separate aliquots taken from the same source. Duplicate samples are analyzed independently to assess laboratory precision.

    1. If the relative percent difference from duplicate sample analyses is greater than 50 percent, then both duplicate samples and the affected batch of samples will be reanalyzed.

5. System Performance

    1. An initial calibration curve is created to demonstrate the linearity of the HRMS system over the calibration range. An initial calibration is repeated once a year, whenever a new set of spiking calibration standards are created or whenever the continuing calibration falls outside the acceptance criteria. To help with the quantitations of high- level samples, a secondary ICAL (concept under evaluation) is available whereby the ES concentrations are 20 times lower compared to the primary ICAL. The secondary ICAL provides RRFs for analytes requiring 20-fold dilutions.

    2. The instrument is tuned to the minimum required resolving power of 10,000 (10 percent valley or 5 percent crossing over) at an appropriate reference signal close to the masses of interests. Document the resolving power using the mass peak profile display. The latter is obtained at the beginning and the end of each analytical sequence of 12 hours or less.

    3. The BCS_3 is prepared at the same concentration as the CS_3 of the ICAL.

        1. It is a new concept introduced to, not only, enhance the accuracy of the measurements, but to provide a basis for assigning an uncertainty to each measurements (Note: this is limited to the measurement step because it does not directly address the sampling errors), and abridge the level of effort involved in the documentation of the system's performance (i.e., what used to require three separate analyses are now combined into one). More details are available in the Performance Commitment document.

            It is prepared—inside a 4oz. glass jar—in stages at the same time as the batch of field samples; i.e., at each phase involving the addition of the ES, CS or AS, JS to the samples. For air samples, the BCS_3 is initiated at the same time as the preparation of the air sampling modules before the sampling session. To that effect, the same amount of the Sampling Standards is added to a vial, which is kept in the laboratory at room temperature and away from light. The corresponding Lab Method Blank prepared with the same batch of sorbent and spiking solution (i.e., 40 g XAD-2 resin, or PUF) is kept refrigerated.

            One BCS_3 per batch of 20 samples or less -- regardless of the matrix type – is going through the same spiking scheme with the same spiking solutions, same analyst, same delivery system, and at the same time as the field samples. It is the laboratory's responsibility to ensure sufficient BCS_3s are prepared to provide front- and back-end calibration verifications for all the samples as well as re-injections when necessary. For air samples returning with multiple trap preparations for a given project, select one of the BCS_3 (i.e., the one representing the largest number of traps) and use it to verify calibration (PD) and stability (RPD). However, use the ICAL RRFs to process all the samples associated with such project if it can be determined that the data reliability is not adversely affected. The laboratory will make every effort to communicate to the stack-sampling firm the significance of the trap preparation in light of the QA/QC.

            The addition of both NS and ES should be performed using the same technique and the same volume. That way, any systematic error associated with the ES (within acceptable limits as defined herein) will "ratio out" when the two BCS_3 calibration analyses are used to compute the analyte concentrations in the samples. By using this approach, the accuracy of the measurements is superior to the traditional approaches. It is also a benefit that flows directly from true stable isotope-dilution GC/MS, which until now was regrettably ignored.

            For air samples where a split factor is involved, i.e., the sample extract is split and a portion is archived as backup, the BCS_3 is not subjected to an actual physical division. The latter is simulated by the addition of an appropriate volume of the same solvent as for the ICAL and the samples (e.g., if the split factor is 2, then, the BCS_3 needs to be diluted two fold before analysis to allow the analytes to be at the same concentration as for the ICAL CS_3).

        The BCS_3 is then analyzed at the beginning and at the end of a NTE 12-H analytical sequence during which samples are analyzed.

        In order to use the front- and back-end BCS_3s averaged RRFs to process the samples, the individual front- and back-end RRFs need to meet a number of requirements (independent verification, RPD, and PD or bias).

        The following criteria for the BCS_3 need to be met:

            1. The first and last PCDD/F eluters are verified to be within the eight homologue retention time windows.

            2. The signal to noise ratio (S/N) exceeds 10:1 for all ions monitored,

            3. The ion abundance ratio measurements are within ± 15 percent of the theoretical ratio,

            4. D. The RRFs Percent Differences (PD) relative to the ICAL should remain within established criteria. These criteria may be established statistically or on a per-project basis, according to the data user's needs. If no criteria are established through negotation with the client or statistically, the following critera are recommended.

Twenty percent for the unlabeled compounds
Thirty percent for the labeled ES compounds
Twenty percent for air's labeled SS, and
Thirty percent for non air's labeled CS compounds
Other requirements are shown in Table Insert 1 and Table Insert 2.

            5. The RPDs between the front- and back-end BCS_3s should remain within the limits established with the client or statistically. In the absence of such criteria, it is recommended to use those summarized in the Table Inserts.

6. As defined above, the criteria for an acceptable BCS_3 are summarized in the table inserts below in the absence of other criteria.

6. Duplicate Analyses (optional)

Ideally, to be meaningful and of value, a duplicate sample is submitted to the laboratory in a blind fashion. This way, their role is not limited to assessing the performance of the analytical aspects but as a whole, the sampling aspects as well. However, should the scope of the particular work requires the laboratory to select a sample as a duplicate, then the results of the laboratory duplicates (concentrations of 2,3,7,8-substituted PCDD/PCDF compounds) should agree with criteria established through negotiation with the client or otherwise derived from project specifications. In the absence of such criteria, the duplicates should agree to within a 25% RPD.

7. Laboratory Method Blank

For a given matrix (i.e., non-biological solid, aqueous, biological tissue, air) a minimum of one Laboratory Method Blank (LMB; mandatory) per batch of 20 samples or less is prepared following the exact same steps as the samples using the same reagents and standards. As part of good laboratory practices, it is recommended that the LMB be extracted on a different extraction position from one batch to the other by tracking and recording the extraction position number of the LMB as well as the associated samples. Similarly when using automated sample fractionation techniques, rotate the position of the LMB from batch to batch, and record that information. For reporting the results, always use the same units and the lowest sample volume or weight from the field samples. Note that, for air samples, the LMB is prepared at the same moment, using the same batch of sorbent materials, spiking solutions and technique, and by the same personnel who prepared the sampling modules before the sampling session.

13. CALIBRATION AND STANDARDIZATION

1. Initial Calibration

1. The ICAL establishes the operating conditions necessary to meet the relative retention time specifications specified in EPA Method 8290/1613. The percent RSD for the mean response factors must be within ± 10 percent for the native standards and within ± 20 percent for extraction standards. Note that these requirements are more stringent than Method 8290 or Method 1613's tolerance windows. In addition, the RRFs must remain within 20 percent of the historical values. All S/N must be at least 10:1. Ion-abundance ratios must be within the 15 percent window of the theoretical ratios. The ICAL used for analytes is summarized in Table 2A.

1. Inject the reference compound perfluorokerosene (PFK). PFK provides the required lock masses and is used for tuning the mass spectrometer.

2. The lock-mass ion from PFK is dependent on the masses of the ions monitored within each descriptor. Each descriptor will be monitored in succession as a function of GC retention time to ensure that all PCDD/PCDFs are detected.

3. An appropriate QC Check Ion will be monitored for each mass descriptor and shall be used to monitor system performance throughout the respective retention time windows. Specific situations where "deflections" are detected are evaluated on a case-by-case basis with emphasis on the impact on the reliability of the analyte data.

2. Continuing Calibration

1. Follow the BCS_3 requirements. Using the same operating conditions as established for the ICAL, inject 1 mL of the batch control spike (BCS_3) at the beginning and end of each 12-hour period during which samples are analyzed in order to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, to establish the PCDD/PCDF retention time windows and isomer-specificities, and to validate the standards and the spiking technique. When true 1613 requirements are required, follow the procedures below.

2. Inject a column performance standard mix (CPSM) to verify retention time windows. This requirement can be accomplished by using the OPR analysis. The latter is prepared with the appropriate congeners. The following criteria must be met:

1. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting isomers must be resolved with a valley of ±10 percent. Note that the method calls for a less stringent requirement of 25 percent. Analytical Perspectives also requires that the peak shape of the TCDD/F be normal before one can use the DB-5MS column for both TCDD/TCDF isomer-specific determinations.

2. The first and last PCDD/F eluters are verified to be within the eight homologue retention time windows.

3. Inject a mid-range standard from the initial calibration curve (CS3) at the beginning and end of every 12 hours. The following criteria must be met:

1. The relative response factors for the mid-range standard are within the limits established in Method 1613. That is, the percent RSD for the mean response factors must be within the method's tolerances.

2. The ion ratios are within 15 percent of the theoretical.

3. The signal to noise ratio (S/N) exceeds 10:1 for all ions monitored.

4. The retention times must be within the criteria established in Method 1613.

14. EXTRACTION AND CLEANUP PROCEDURES

1. Extraction

1. Determine the percent solids on all samples the day before, except for oil. Weigh out an appropriate weight or volume, dry overnight in 110 °C oven and re-weigh.

2. All samples are extracted on a wet weight basis. For solid samples, adjust the sample amount for extraction to yield a 10-g equivalent dry weight based on the percent solids.

3. In general, if samples are "dirty" or samples contain oil or fuel oil, all cleanup steps may be required.

4. Add the Extraction Standards and native spike (A x) as described in the sample path forms. When appropriate use 1 mL of acetone for spiking.

5. Aqueous or Effluent Samples: If the sample contains >1.0 percent solids, treat the sample as a solid (i.e., isolate a cake). Aliquot an amount of the aqueous sample that will yield a 10-g dry weight equivalent. Filter this aliquot thru a 1.0 mm filter using the filtering setup. Transfer the filter and cake inside the thimble. Spike the appropriate standards using acetone as a carrier. Add 10 g Hydromatrix TM and mix the solids from the filter through the Hydromatrix TM. If solids are still present in the water phase filter the water through 0.7 mm and 0.45 mm filters removing and placing them in the

same glass thimble. This insures a complete recovery of the 10-g dry weight equivalent.

If the solid load is less than 1.0 percent, the sample may be extracted using the TALEX, CLL , or the SPE-C approaches. The details for these procedures are given in the AP-SP-E analytical procedures. The decision to follow one particular approach over the others is dictated by the client's requirements, the type of samples undergoing analysis, and the expertise of the laboratory Director.

Note: All paper mill effluent samples should be filtered, the isolated solids extracted by SPE and SDS.

6. Solid or Waste Samples: Add 10 g of sample directly into an 8oz jar, add 5% H_2SO_4 until the sample is easily stirred and wet enough for additional liquid to be easily dispersed, spike in acetone, mix sample well, mix with Hydromatrix TM. Soxhlet/Dean Stark extract for 16 hours with toluene (250 mL C 14). Proceed with appropriate cleanup procedures described in section 8.2.

    1. To separate phases of wet (>25 percent water) soil, sediment or paper samples, a Soxhlet/Dean Stark extractor system may be used with toluene as the solvent.

7. Oil Samples: Dilute the sample with 50 mL of hexane. Proceed with appropriate cleanup procedures described in section 8.2.

8. Air Samples: Each sample is usually comprised of a filter, a XAD-2 resin trap, solvent rinses. (Note: aqueous impinger contents and catch for samples are part of CARB Methods 428 & 429.) Samples being prepared by EPA Method 23 are comprised of a filter, a XAD-2 resin trap, solvent rinses and the toluene rinse, which is prepared separately if requested. Method 0023A requires the filter/front half and the XAD-2 resin trap/back half to be extracted separately and analyzed by Method 8290. For ambient air samples, a PUF and filter combination is typical.

    1. Filter and XAD-2 resin trap should be photographed together for documentation purposes prior to combination (Method 23). Line up components next to the corresponding thimbles and take a group photograph, and then take a photograph of each sample's components immediately before combining into the thimble.

    2. Combine resin and filter in a SDS extractor. **Use glass thimbles in lieu of cellulosic thimbles. Cellulose thimbles are known to react with chlorine leaching out of the resin from high-chlorine sources to form 2,3,7,8-TCDF.**

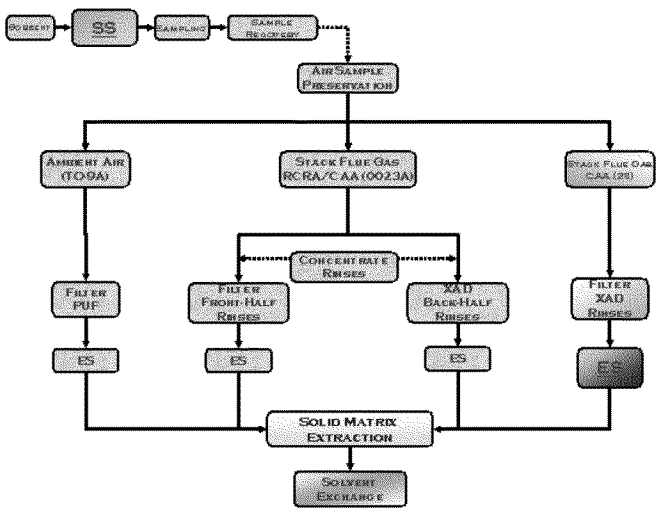
    3. Concentrate the rinses to less than 5 mL using a rotovap or by other appropriate means. Add concentrated solvent rinses to resin/filter portion in thimble . **An alternative for concentrating probe rinses consists of adding 50-100 m L of tetradecane to each container. Remove the cap and keep it in front of the container until it is time to cover the container. Make sure that all containers are properly labeled before initiating the concentration. Allow the solvent to evaporate inside the hood for 24 H or so. Do not allow the evaporation to go beyond "dryness" for extended periods of time (i.e., 36 H or more) and do not perform activities inside the hood that could contaminate the samples. Ideally, this is carried out during the nighttime. Use the rotovap when time is of essence.**

    4. Into the thimble, spike the appropriate amount, as indicated on the sample path tracking sheets of 23 D/F Extraction Standards. Place extractor atop of a 500-mL round-bottom flask containing Teflon TM boiling chips, and 350 to 400 mL of toluene.

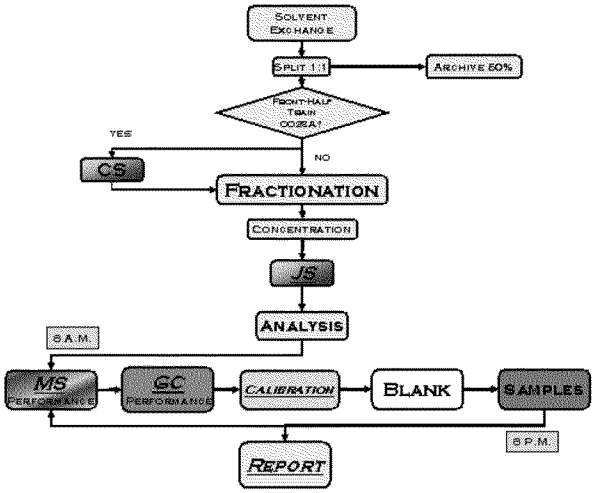
    5. Place a glasswool plug into the thimble on top of the resin. Assemble the entire SDS apparatus to the condenser and place upon heating mantle. Turn on the heating units, cooling water and set temperature for toluene to boil. Allow refluxing for 16 hours at the rate of 3 cycles per hour.

    6. **Before turning off the heaters, allow the toluene to drain from the Dean-Stark arm directly inside a waste bottle. Distill off the toluene until you reach a volume of about 50 mL inside the boiling flask. Once the unit is cooled, add the Alternate Standard. Split the sample in half and further concentrate the residue. Proceed to Clean-up.**

    7. Splitting: Transfer the extract residue with hexane inside a calibrated 15-mL centrifuge tube. Use a total of 12 mL and divide the sample extract in half unless otherwise noted on the process sheet. Store at room temperature the archived portion in the centrifuge tube with a Teflon TM-lined screw top.



Sample Preparation Flow Chart for Air Matrices



Sample Analysis Flow Chart
(example given for air matrices)

9. Tissue Samples: Tissue samples are ground and homogenized. Others can be used as such.
    1. Grind fish using the Hobart meat grinder. Collect the ground tissue directly on cleaned aluminum foil.
    2. Using Tissuemizer blend meat into a creamy paste consistency.
    3. Using a spatula, mix well.
    4. Place two 25-g aliquots of the ground tissue inside two 4-oz jars, label the jars and store in a freezer.
    5. Aliquot another 25 g for analysis or on such requested occasions, aliquot 75 g.
    6. Fortify directly on matrix using acetone as the carrier.
    7. Mix with 20-25 g of Hydromatrix TM , stir until a dry, free-flowing consistency is achieved, adding more Hydromatrix TM as needed, careful not to exceed an amount that can fit into the acid thimble for 25-g sample sizes. Place the mixture on top of a layer of **acid-coated silica gel inside a glass thimble for the pre-cleanup step** (*vide infra*). **The amount of acid-coated silica gel is dependent on the lipids contents. Typically, 50 g are used. Prime the acid-coated silica the day before with hexane.**
    8. For 75-g samples , **the acid thimble is not used.** The sample is extracted as is with Hydromatrix TM and the oversized extraction setup is used in this case to ensure that enough solvent is used and that there is enough room in the thimble to allow for proper extraction of the sample.
    9. Spike each extraction cell with the appropriate Extraction Standards.
    10. Soxhlet Dean-Stark using hexane for 16 H. For the rare 75-g samples, however, a mixture of 30% Acetone and 70% Toluene should be used rather than Hexane. Again this is to ensure a proper extraction is achieved! Note that when PCBs are extracted as well as PCDD/Fs, the solvent mixture is hexane – acetone (1:1). In case the tissue contains sediment particles, it is recommended to follow the hexane-acetone extraction with a toluene-acetone extraction. Whenever a 75-g sample is extracted, the extraction time is extended from 16 H to 60 H.
    11. Concentrate the extract **utilizing the SDS down to ~100 mL then finish the concentration** on the Rotovap
    12. Add the CS.
    13. ASECS (sample extract using SOP AP-SP-CU1 current revision).

The section below was, during a recent revision of our SOPs, inserted in the SOP for Homogenization, which should be limited to homogenization. It is transferr because of the nature of the solvent used for different parameters.

EXTRACTION of Fish Tissue

- After tissuemizing, aliquot 25-g in an 8-oz jar and a separate 5-g in a 40-mL VOA vial for analysis and lipid determination, respecti each "reportable sample", two 25-g backup samples are prepared in 4-oz jars at the same time as the samples undergoing analysis (If are required, three 25-g backup samples are prepared). The weight is recorded on the outside of the jar and they are kept inside a free maintained at –18 o to –20 oC for future use. Typically, they are kept for a 1-year period following the submission of the report.
- **Whenever the need to engage such archived sample arises, it is important to quantitatively transfer the entire contents of the container inside the extraction vessel. The rationale is that freezing tissues will result in breaking the cells releasing water and We must ensure that all the water and lipids leaching out are included in the analysis or it will be impossible to reproduce the Use the weight that was recorded at the time the archive was prepared.**
- Fortify the sample with the ES using acetone as a carrier. Stir the fortified sample using a spatula to mix the spike into the tissue. Ad Na 2SO 4 to each sample so as to obtain a "dry", free flowing sample.
- Transfer the sample to a **prepared/presoxed in hexane acid coated silica** thimble for 8290B analysis **or Petroleum ether for WH PCB analysis only (see below for preparation of acid coated silica thimble).**
- Perform an SDS extraction using hexane with **0.25 mL of tetradecane** for 8290B **or Pet Ether for WHO-2 and PCB analysis** for
- After the extraction, fortify the extract with the CS and rotovap to ~3 mL
- Perform the ASECS and prepare sample for GC/MS.

PREPARATION OF ACID COATED SILICA THIMBLE for SDS of Tissues

- **Select a large glass fritted thimble**
- **Place a 0.7- m m filter in bottom of thimble so as to completely cover the glass frit.**
- **Weigh 2-g of furnaced silica gel in a small 100-mL beaker and transfer to the thimble, covering the filter in the bottom of the**
- **Weigh 50-g of acid coated silica in a separate beaker and transfer on top of the 2-g silica layer in the thimble**
- **Weigh additional 2-g of furnaced silica and cover the acid coated silica layer in the thimble**
- **Soxhlet 16H in hexane or Pet Ether to clean and prewet the silica gel. Prewetting allows for easier refluxing of the sample wh to the thimble.**
- **After soxhlet, dismantle Dean Stark and thimble holder glassware and wrap pieces in foil (shiny side out) for reuse during ex of samples. Do not reuse the solvent or round bottoms.**

2. Cleanups **(note: refer to specific SOPs for the latest version; this Core Method SOP may not contain the same level of details)**.
    1. If not done, add the Cleanup Standards. Rotovap to C_{14}. Proceed to first cleanup.
    2. ABP-Acid/base partitioning ("dirty" samples only)
        1. Acid/Base Silica Column (see SOP AP-SP-CU1 current revision)
        2. **Florisil Column** (see SOP AP-SP-CU1 current revision)
3. GC/MS ANALYSIS
    4. Establish the necessary operating conditions. The following GC operating conditions are for guidance and adjustments may be required.

Injector temperature:	280°
Interface temperature:	270 °C
Initial time:	2 minutes at 190°C
Temperature program:	200 to 220 ° C, at 5 ° C/min
	220 ° C for 14.5 minutes
	220 to 290 ° C, at 5 ° C/min
	290 ° C for 1 minute
	290 to 305 ° C, at 10 ° C/min
	305°C for 10 min

    1. The reference compound perfluorokerosene (PFK) provides the required lock masses and is used for tuning the mass spectrometer.
        1. The lock-mass ion from PFK is dependent on the masses of the ions monitored within each descriptor. Each descriptor will be monitored in succession as a function of GC retention time to ensure that all PCDD/PCDFs are detected.
        2. An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ±20 percent throughout the respective retention time window.
        3. The mass resolution check is achieved before any analysis is performed and at the end of each 12-hour shift.
    2. Set up the analytical run following this sequential injection pattern: CPSM-CS3, Solvent Blank, Method Blank, Samples, OPR, or BCS_3, Solvent Blank, Samples, BCS_3. (The solvent blank spiked is spiked at a concentration of 1 pg/µL.
    3. Qualitative Determination
        1. To identify a chromatographic peak as a PCDD or PCDF (either an unlabeled or a labeled compound). It must meet the following criteria:
            1. The signals for the two exact m/z being monitored must be present and must maximize within ±2 seconds of one another.
            2. The signal-to-noise ratio (S/N) of each of the two exact m/z must be greater than or equal to 2.5:1 for a sample extract, and greater than or equal to 10:1 for a calibration standard.
            3. The ion abundance ratios must have a ratio within the limits established for the homologous series.
            4. The absolute retention times for non-2,3,7,8-substituted congeners must be within the corresponding windows set by the CPSM.
            5. The absolute retention times for 2,3,7,8-substituted congeners must be within 0 to +2 seconds of the isotopically labeled standard; these new limits are derived from over 500 data points obtained from MM1 and MM3 over a 17-week period worth of BCS_3 and CS3/CS0. The 99% confidence intervals suggested 0 to 1 sec.; AP decided to use 2 sec. to cover all analytes (updated on 17 OCT 07). These limits are more representative of our level of performance. Weak peaks will continue to be treated as before with the call made by the chemist.
            6. To clarify the situation regarding processing of the following potential co-eluters in DF processing:
                1. **23478**/12489-PeCDF
                2. **234678**/123689-HxCDF
                3. **123789**/123489-HxCDF

            Each of these co-eluters present a problem with processing since they can either be treated as independent (i.e. resolved) peaks or as a

combined peak pair – the issue is that determining a TEQ from these peaks cannot be done if treated as a pair. This was considered as a future software development, but it hasn't occurred because of the need to match up with client EDDs that have no concept of a peak partially contributing to the TEQ. Therefore, although the software (both UTP and the DF macro) allow each of these to be treated as peak pairs, this should not currently be used.

This note outlines the procedure that should be followed.

For 23478/12489-PeCDF: this occasionally shows a point of inflection that would allow a vertical to be dropped distinguishing the two separate peaks (with the appropriate PR flag), but in most cases this peak should be treated as the specific only (i.e. just 23478-PeCDF) so that it does contribute to the TEQ. (A PR flag should still be used on the chromatogram even if the peak is designated as 23478-PeCDF, but the co-eluter is clearly also present).

For 234678/123689-HxCDF: these are never resolved (on a *-5ms column) and so should always be quantified as the specific (i.e. 234678-HxCDF).

For 123789/123489-HxCDF (the "last" HxCDF eluter): this situation is slightly more difficult since, in samples, the peak is often actually due to the non-specific 123489-HxCDF. This is evident from the notable shift in retention time relative to the CPSM/BCS3 (or indeed, the RRT relative to the ES-123789-HxCDF). It therefore becomes the analyst's call as to which peak it is assigned as, and whether a PR flag should be used, but it is particularly important to be consistent across all data. The method actually allows the specific to be -1/+3 seconds relative to the ES, and this can also be used as guidance.

4. Quantitative Determination

    1. For peaks that meet the criteria listed above, quantitate the PCDD and PCDF peaks from the mean RRF relative to the appropriate Extraction Standard established in the initial calibration.

    2. Recovery of each Extraction Standard versus the Injection Standard should be between 40-135 percent or have a signal to noise ratio >10:1 and a favorable detection limit (Method 8290). See Method 1613 for the acceptable windows.

    3. It is recommended that sample recoveries less than 40 percent or greater than 135 percent be re-extracted and re-analyzed unless the S/N ratio is >10:1 and/or the DL is unacceptable. Similarly, outliers from Method 1613 tolerances should be considered for re-extraction. However, the Lab Director has the option to accept the data provided they meet our extraction requirements. Re-extraction is always required if we can show that the deviations result from an action that can adversely affect the data reliability. See the Decision Flow Charts for the "*Thinking Method*".

    4. Report results in picogram per gram, picogram per liter or picogram per sample.

    5. Any sample in which the 2,3,7,8-TCDF is identified by analysis on a DB-5 GC column and is above the method calibration limit must be confirmed on a DB-225 or equivalent GC column. The use of the DB-5MS for both 2,3,7,8-TCDD and 2,3,7,8-TCDF isomer specificities can also be used. However, the percent valley for 2,3,7,8-TCDD is more stringent (10 percent instead of 25 percent) and the TCDD/TCDF peak shape must be normal (i.e., no tailing) to allow accurate measurement of the 2,3,7,8-TCDF isomer on the DB-5MS column. Analytical Perspectives can provide additional documentation on the validation of the DB-5MS for 2,3,7,8-TCDF determinations. Alternatively, the demonstration of isomer specificity is conducted in conjunction with the BCS_3 analyses (enfolded performance).

    6. For 2,3,7,8-substituted congeners that are not identified, calculate a sample- and analyte-specific estimated detection limit.

    7. For a homologous series with no positive identifications, calculate the detection limit.

    8. Click here for more information on "Working at the Limits".

15. DATA ANALYSIS AND CALCULATIONS

1. The concentrations for the PCDD or PCDF compounds are calculated by using the formula:

$$C_X = \frac{A_X \times Q_{is}}{A_{is} \times W \times RRF}$$

Where

C_X = Concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g.

A_X = Sum of the integrated ion abundances of the quantitation ions (See Table 6 of EPA Method 8290) for unlabeled PCDD/PCDFs.

A_{is} = Sum of the integrated ion abundances of the quantitation ion (See Table 6 of EPA Method 8290) for the labeled Extraction Standards.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

W = Weight of the sample (solid or liquid).

RRF = Calculated relative response factor for the analyte.

2. The detection limits for each absent 2,3,7,8-substituted PCDD/PCDF can be calculated using the following formula:

$$DL = \frac{2.5 \times H_N \times Q_{is}}{H_{IS} \times W \times RRF}$$

DL = Estimated detection limit for homologous 2,3,7,8-substituted PCDD/PCDFs.

H_N = Noise height (peak to peak).

H_{IS} = Peak height of the Extraction Standard.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

W = Weight of the sample (solid or liquid).

RRF = Calculated relative response factor for the analyte.

16. METHOD PERFORMANCE

1. The method performance is thoroughly documented in our Statement of Performance, which includes the results of performance testing studies, audit samples, and international interlaboratory calibration studies.

17. POLLUTION PREVENTION

1. See Pollution Prevention Basics

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

1. This method is performance-based. Thus, the acceptance criteria are ideally determined by the project needs through a process of negotiation with the client and any other ultimate end-user of the data. These criteria should ensure that the performance of the method is adequate for the purposes for which it is intended. The criteria will likely not resemble those used in the past. In the absence of such criteria, those outlined elsewhere within this SOP and within the published methods may be used.

2. 2. A failure to meet all criteria does not necessarily result in a particular course of action (see next section for details). Data assessment includes a thinking process that assesses the impact of a particular analytical problem and develops the most appropriate response, in the context of the data users needs (when known). Data that do not meet all criteria for all target analytes may still be reported with relevant qualifiers and notes in the case narrative, if appropriate.

19. CORRECTIVE ACTIONS

1. Corrective actions are taken whenever needed, regardless of acceptance criteria. It is not always the case that data meeting all acceptance criteria should be accepted nor that data not meeting all criteria should be rejected.

2. 2. When the BCS3 fails, it is important to discern the following:

    1. The fundamental objective of the BCS_3 is to "validate" the standard solutions and spiking technique and the RRFs used to quantitatively characterize the analytes in the samples **at the time** the standards are used to prepare and analyze the samples. They are four types of standards involved in the preparation of the BCS_3 that provide various probes into assessing this "validation" procedure. They are the NS (symbolized as A_x in expressions or tables), ES, SS or CS, and JS. The question becomes how can one "extract" the information needed to complete the validation, or how does one "filter" out the irrelevant information to help with the distinction between a critical error and a minor one. A critical error means erroneous data resulting from a seriously flawed spiking technique (e.g., wrong amount of ES added under the OPR/LCS/ICAL system, or the NS under the BCS_3 system) while other minor errors can provide useful information or feedback on the measurement step (e.g., instrumentation variation). The interpretation of the information obtained from the analysis of the BCS_3 is best handled when done contextually. This analytical protocol does not claim that it offers a comprehensive analysis but merely puts forward guidelines to help the analyst in assessing the quality and reliability of the data.

    2. A failure on the "PD" requirements may be indicative of an instrumentation difficulty or spiking error. The latter can be of Level PD-1 (i.e., at the standard solution level) or Level PD-2 (i.e., at the spiking operation level). A third Level PD-3 is associated with instrumentation. An error at the NS standard solution level (Level PD-1) constitutes, under the BCS_3 system, the most serious failure and requires that a new set of standard solutions be prepared and independently validated before repeating the sample extraction and analysis, if called for by the decision flow chart ("*Thinking Method*"). Note that the decision flow charts make a distinction between short- and long-term actions. When appropriate, a new initial calibration may be required before analyzing the BCS_3 and the samples. However, if the error is a Level PD-2 error, a re-extraction and analysis is the most suitable action after correcting the flawed spiking technique. As customarily done, a new BCS_3 is prepared with a Level PD-2 error. Here again, the decision flow charts should be used since the text herein is only for illustration purposes. Distinction between Levels PD-1 and PD-2 can be accomplished contextually by examination of the initial independent validation study and control charts (showing for instance a trend suggesting a degradation of the ES solution), behavior over time charts, and/or using the matrices shown in Table Inserts 3 or 4. The Level PD-3 error is associated with instrumentation when an out-of-calibration situation is present or a temporary or localized instrumentation variation is operative. Depending on the severity of the Level PD-3 error, a new calibration (either ICAL or rerunning the BCS_3 and all the affected samples) following a new "tuning" of the instrumentation may be required (see Decision Flow Charts for "*Thinking Method*").

    3. A failure on the "RPD" requirements may be indicative of instrumentation instability or inability to sustain the instrumentation's performance over a 12-H period. Again, two levels are possible. Level RPD-1 is strictly associated with instrumentation difficulties that are unrelated to the samples under analysis. A re-analysis (i.e., re-injection) of the BCS_3 **and** of the samples can be considered as a corrective action after correction of the source of the instrumentation's shortfall (see Decision Flow Charts for "*Thinking Method*"). If

however, the re-analysis of the BCS_3 fails again, and there are indications that the spiking procedure is questionable (Level PD-1 or PD-2), the associated extraction batch may need to undergo re-extraction and analysis with the preparation of a new associated BCS3 as discussed above for the BCS_3 PD deviations. A Level RPD-2 BCS_3 failure may be found with the analysis of samples presenting special challenges (i.e., highly complex matrices that do not cleanup well under the various options offered by this protocol). Depending on the severity of the deviation, additional cleanup or other appropriate actions may be required before re-analysis of the samples and associated BCS_3. If such action proves to be ineffective, the data should be qualified accordingly.

4. A " **PD**" failure for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF results in the inability to reliably quantify 2,3,7,8-TCDD/F until proper corrective action is implemented (e.g., following GC column maintenance). When the corrective action involves a different GC column liquid phase, the **correct** BCS_3 is used to demonstrate adequate performance. Note that the laboratory is encouraged to adopt a similar stance for 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF (or any other 2,3,7,8-subtituted congeners, which significantly contribute to the TEQ and have other congeners closely eluting to them).

5. The BCS_3 "PD Requirements" are summarized in the four table inserts below. In addition to the traditional RRFs, another set of "pseudo-RRFs" is computed from the BCS3 data to help with the validation of the ES and RRFs used to report the sample analytes. The pseudo-RRFs are used to further differentiate the various "A" to "C" types PD Requirements. Use Table Insert 3 (non air) or Table Insert 4 (air) for departing-from-the-norm groups of analytes (e.g., all 17 A x or the five SS show a deviation similar in "sign" and "amplitude"). It is also recommended to examine the data contextually (e.g., using QC charts)

Table Insert 1:

Batch CS_3 PD Requirements

Based on Traditional RRFs

("A" to "C"Types)

Type	Analytes	Requirement	Failure Possible Cause[a,b]	Failure Level	Suggested Corrective Action
A	A_X vs ES	+ 20%	1. Calibration out 2. Spiking error	1. PD-3 2. PD-1/PD-2	3. New Calibration 4. New Standards/New Extraction
B	ES vs JS	+ 30% non air + 30% for air[c]	1. Calibration out 2. Spiking error	5. PD-3 6. PD-1/PD-2	7. New Calibration 8. New Standards/New Extraction
C_1	CS vs JS	+ 30%	1. Calibration out 2. Spiking error	9. PD-3 10. PD-1/PD-2	11. New Calibration 12. Affects other Types
C_2	SS vs ES (air)	+ 20%	1. Calibration out 2. Spiking error	13. PD-3 14. PD-1/PD-2	15. New Calibration 16. New Standards/New Extraction/New Sampling[d]

a. Calibration out = usually when one (localized) or several/all analytes are affected; instrumental source.
b. Spiking error = when all analytes are affected with the same "sign" and "amplitude"; must be considered contextually; i.e., using historical data or other information on the set of standards such as the "pseudo-RRFs". Situations when selected analytes degrade are rare but should not be excluded from consideration.
c. By design for air matrices, the amounts of ES and JS added during the preparation of the Batch CS 3 are different. Thus, an additional error is introduced, which can deceive the analyst's interpretation. In this case, the QC emphasis is shifted towards the "C2" type PD requirement.
d. Because of the nature of an "air" sample, there is no additional sample volume available to repeat the extraction. The laboratory is required to qualify the data by estimating and documenting accordingly the "error" associated with the reported measurements. If such documentation is not possible, and/or the information points toward a seriously flawed ES addition (as opposed to a spiking error associated with the SS), the data can be rejected and re-sampling efforts may be necessary. See the "Air Spiking Related Error Matrix" tables for an alternative approach whereby the A_X vs SS RRFs are used to determine the analyte's concentrations (Table Insert 4).

Table Insert 2 :

Batch CS_3 PD Requirements

Based on Pseudo-RRFs

("D" to "G"Types)

Type	Analytes[a]	Requirement
D	A_x vs **CS/SS**	+/- 25%
E_1	A_x vs **JS** (non air)	+/- 35%
E_2	A_x vs **JS** (air)	+/- 35%
F_1	**ES** vs **CS** (non air)	+/- 20%
G_2	**SS** vs **JS** (air)	+/- 50%

a. Pseudo-RRFs are limited to analytes, for which an analogous/homologous standard is available:

- 2,3,7,8-TCDD (A_X) vs $^{13}C_{12}$-1,2,3,4-TCDD (JS)
- 2,3,4,7,8-PeCDF (A_X) vs $^{13}C_{12}$-1,2,3,4,6-PeCDF (CS)
- 13 C 12-1,2,3,7,8-PeCDD (ES) vs $^{13}C_{12}$-1,2,3,4,7-PeCDD (CS)
- Do not consider pairs such as OCDD (A_X) vs $^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF (SS) or $^{13}C_{12}$-1,2,3,4,7-PeCDD (CS or SS) vs $^{13}C_{12}$-1,2,3,4,6,7-HxCDD (JS)

Table Insert 3:

"Non-Air" Spiking Related PD Errors

(departing-from-the-norm group of analytes)

"PD Requirements Decision Matrix" – Normal Configuration
(use BCS_3 RRFs)

	Ax	ES	CS	JS
Ax	-	Y	Y	Y
ES	-	-	Y	Y
CS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective A_x Spiking = Fatal
(If A_x spiking is shown to be in error, and if no additional or replacement sample is available, use ICAL RRFs if CS_3 is acceptable)

	Ax	ES	CS	JS
Ax	-	N	N	N
ES	-	-	Y	Y
CS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective JS Spiking
(use BCS_3 RRFs)
percent recovery measurements for CS & ES affected, not the analytes

	Ax	ES	CS	JS
Ax	-	Y	Y	N
ES	-	-	Y	N
CS	-	-	-	N

"PD Requirements Decision Matrix" – Defective CS Spiking
(use BCS_3 RRFs)
percent recovery measurements for CS affected, not the analytes

	Ax	ES	CS	JS
Ax	-	Y	N	Y
ES	-	-	N	Y
CS	-	-	-	N

"PD Requirements Decision Matrix" – Defective ES Spiking
(use BSC_3 RRFs; see Levels PD-1 or PD-2)

	Ax	ES	CS	JS
Ax	-	N	Y	Y
ES	-	-	N	N
CS	-	-	-	Y

Table Insert 4:

"Air" Spiking Related PD Errors

(departing-from-the-norm group of analytes)

"PD Requirements Decision Matrix" – Normal Configuration
(use BCS_3 RRFs)

	Ax	ES	SS	JS
Ax	-	Y	Y	Y
ES	-	-	Y	Y
SS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective A_x Spiking = **Fatal**
(If Ax spiking is shown to be in error, and if no additional or replacement)

	Ax	ES	SS	JS
Ax	-	N	N	N
ES	-	-	Y	Y
SS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective JS Spiking
(use BCS_3 RRFs)
percent recovery measurements for ES affected, not the analytes or the SS

	Ax	ES	SS	JS
Ax	-	Y	Y	N
ES	-	-	Y	N
SS	-	-	-	N

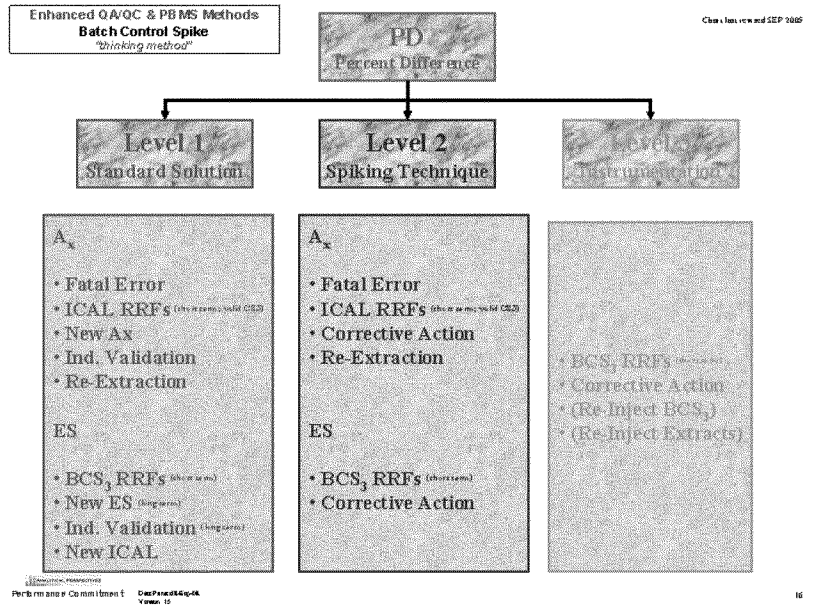
"PD Requirements Decision Matrix" – Defective SS Spiking
(use BCS_3 RRFs)
percent recovery measurements for SS affected, not the analytes

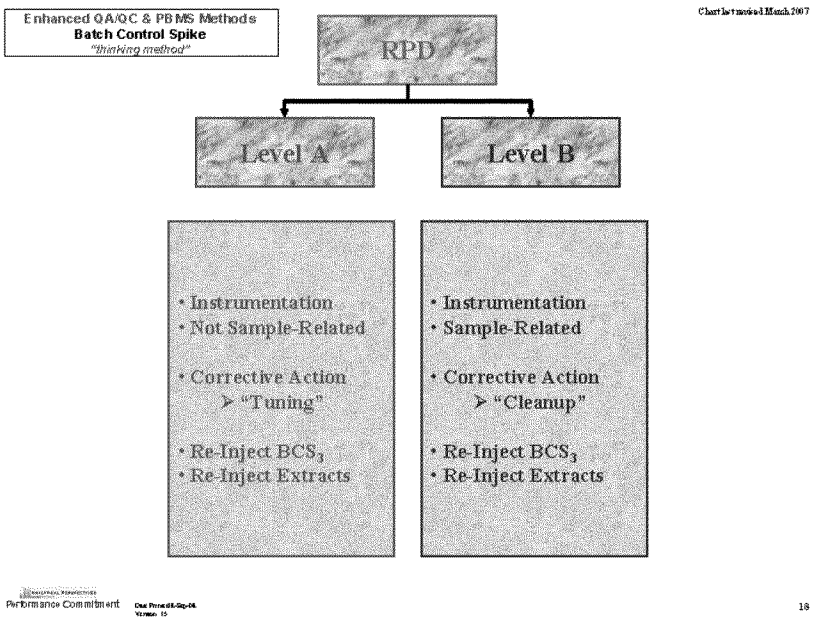
	Ax	ES	SS	JS
Ax	-	Y	N	Y
ES	-	-	N	Y
SS	-	-	-	N

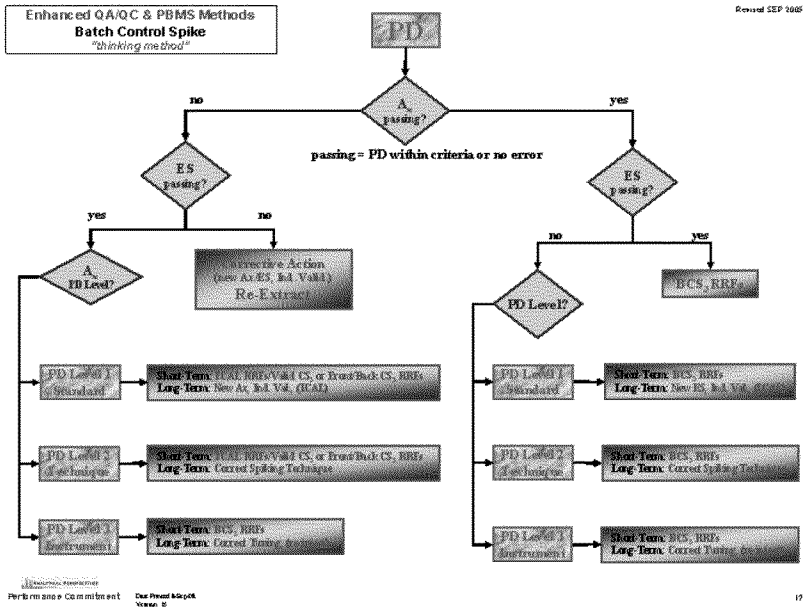
"PD Requirements Decision Matrix" – Defective ES Spiking
(use BCS_3 RRFs; see Levels PD-1 or PD-2; for air samples only, consider using the A_x vs SS RRFs)

	Ax	ES	SS	JS
Ax	-	N	Y	Y
ES	-	-	N	N
SS	-	-	-	Y

2 Decision Flow Charts for "*Thinking Method*"







20. CONTINGENCIES FOR HANDLING OUT -OF-CONTROL OR UNACCEPTABLE DATA

1. Should data be found unacceptable after a thorough assessment, the appropriate corrective action will be taken. In the case that the appropriate corrective action requires reextraction of exhausted samples, the client will be contacted for consultation with regard to the next steps to be taken.

21. WASTE MANAGEMENT

1. The storage and disposal of wastes generated by this method is covered in our Health and Safety SOPs.

22. REFERENCES

USEPA Method 8290, Revision 0, Dated September 1994.

USEPA Method 8290B, Dated July 2002.

USEPA Method 1613, Revision B, Dated October 1994.

23. TABLES AND NOTES

TABLE 1: Theoretical Ion Abundance Ratios and Control Limits for PCDDs and PCDFs

Number of		Theoretical	Control Limits	
Chlorine Atoms	Ion Type	Ratio	Lower	Upper
4	$^{M+2}/_{M+4}$	0.77	0.65	0.89
5	$^{M+2}/_{M+4}$	1.55	1.24	1.86
6	$^{M+2}/_{M+4}$	1.24	1.05	1.43
6 a	$^{M+2}/_{M+4}$	0.51	0.43	0.59
7 b	$^{M+2}/_{M+4}$	0.44	0.37	0.51
7	$^{M+2}/_{M+4}$	1.04	0.88	1.20
8	$^{M+2}/_{M+4}$	0.89	0.76	1.02

(a) Used for 13C-HxCDF (IS) only.

(b) Used for 13C-HpCDF (IS) only

TABLE 2A: PRIMARY HIGH-RESOLUTION CONCENTRATION CALIBRATION SOLUTIONS

(Regular Initial Calibration)

Concentrations in pg / µL	CS0	CS1	CS2	CS3	CS4	CS5	CS6
Unlabeled Analytes							
2,3,7,8-TCDD	0.26	0.5	2	10	40	200	800
2,3,7,8-TCDF	0.26	0.5	2	10	40	200	800
1,2,3,7,8-PeCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8,9-HpCDF	1.25	2.5	10	50	200	1000	2500
OCDD	2.5	5	20	100	400	2000	5000
OCDF	2.5	5	20	100	400	2000	5000
Extraction Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,7,8-TCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8-PeCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,4,7,8-PeCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-OCDD	10	10	10	10	10	10	10
$^{13}C_{12}$-OCDF	10	10	10	10	10	10	10
Cleanup/Spiking Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	-	0.5	2	10	40	200	-
$^{13}C_{12}$-1,2,3,4,7-PeCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,8-PeCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,9-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF	100	100	100	100	100	100	100
Injection Standards							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4-TCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HxCDD	100	100	100	100	100	100	100

TABLE 2B: SECONDARY HIGH-RESOLUTION CONCENTRATION CALIBRATION SOLUTIONS (optional)

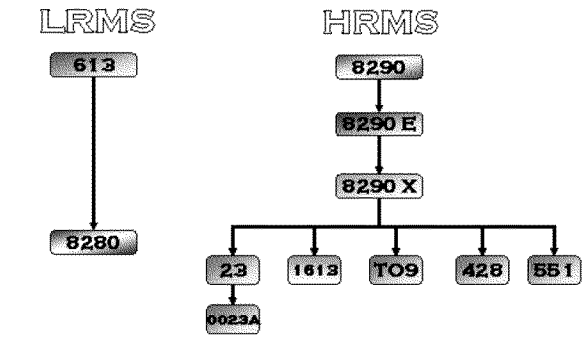
	CS0	CS1	CS2	CS3	CS4	CS5	CS6
Unlabeled Analytes							
2,3,7,8-TCDD	0.25	0.5	2	10	40	200	800
2,3,7,8-TCDF	0.25	0.5	2	10	40	200	800
1,2,3,7,8-PeCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8,9-HpCDF	1.25	2.5	10	50	200	1000	2500
OCDD	2.5	5	20	100	400	2000	5000
OCDF	2.5	5	20	100	400	2000	5000
Extraction Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,7,8-TCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8-PeCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,4,7,8-PeCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	5	5	5	5	5	5	5
$^{13}C_{12}$-OCDD	10	10	10	10	10	10	10
$^{13}C_{12}$-OCDF	10	10	10	10	10	10	10

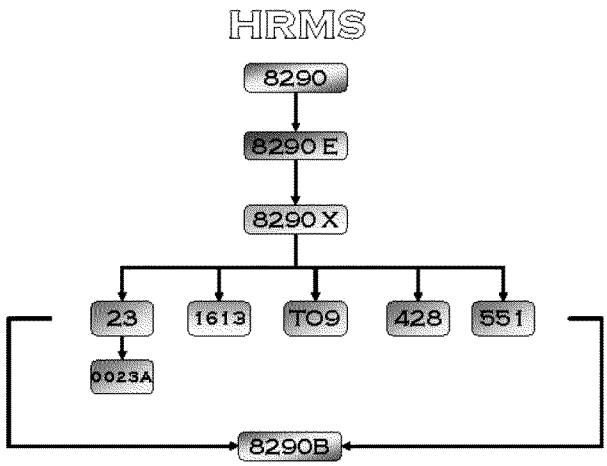
(Initial Calibration used for High-Level Samples Requiring 20-Fold Dilution of the Extract)

Methods 8290 / 1613 / 23 / 0023A / TO9

Method 8290—the first high-resolution gas chromatography and high-resolution mass spectrometry method (HRGC-HRMS)—was introduced by the USEPA in 1985. It is capable of measuring low levels of PCDD/Fs in a variety of matrices in support of the RCRA/CERCLA (Superfund) programs. Towards the end of the eighties, the importance and value of HRGC-HRMS were recognized not only in the US but abroad as well.

Method 8290 underwent a number of changes. The changes—designed and implemented by the original author of the method in a commercial environment—led to a series of new analytical protocols in support of different regulatory programs within the Agency. For instance, Method 23—derived from Method 8290X—is the required protocol for the determination of PCDD/Fs in stack emission samples. Similarly, Method TO9-A for PCDD/Fs in ambient air samples is mostly adapted from Method 23. The SDWA and the CWA programs developed Method 1613, which is also derived from Method 8290X.





All of the above HRGC-HRMS methods are designed to measure PCDD/Fs. They are based on the same technology; i.e., isotope-dilution HRGC/HRMS. The sample extraction, fractionation and calculation procedures are essentially the same. Overall, the methods' performance (e.g., detection limits, precision, accuracy) is the same. What differentiate them are primarily the QA/QC requirements. For instance, Method 8290 recommends a recovery ranging from 40 to 130 percent regardless of the Extraction standard. On the other hand, Method 1613 specifies a different limit for each Extraction standard (e.g., 25 to 164 percent for 13C 12-2,3,7,8-TCDD; 17 to 157 percent for 13C 12-OCDD). Similarly, the calibration acceptance criteria for Method 8290 are different than those defined in Method 1613 (e.g., for the 13C 12-OCDD's RRF in the continuing calibrations, M1613 specifies a tolerance window ranging from –52 to 215 percent while M8290 requires a +30 percent window).

The published Method 8290 only calls for nine Extraction Standards to be added at the extraction stage. Method 1613 identifies 15 Extraction Standards. However, most laboratories, who recognize the fact that Method 8290 was developed at a time when there was a limited number of Extraction Standards, are in effect using a larger set of Extraction Standards, even surpassing the one specified in Method 1613 (see our comments at the end of this document). Just like in Method 1613, most laboratories will use the 37Cl 4-2,3,7,8-TCDD as a cleanup standard for Method 8290 analyses, even though, such standard is not described in Method 8290.

In essence, and to the benefit of the User, i.e.,

1. Improved quality,
2. Streamlined operations,
3. Cost control, and
4. Shorter cycle times

most qualified laboratories have adopted a "universal" methodology whereby the "best" features from each analytical protocol are merged. It was only in the middle of 2008 that we found that our closest competitors finally adopted the use of all 17 13C 12-PCDD/F standards when in fact; AP had been doing this since 2001 along with a number of additional standards (e.g., seven cleanup standards, three injection standards).

This section describes key aspects where modifications and improvements have been implemented by Analytical Perspectives for Methods 8290, 1613 and 23/0023A.

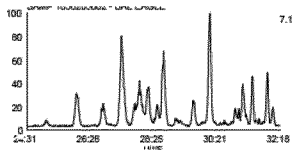
2.1 Relevant Modifications & Improvements to the Published Methods 8290/1613/23/0023A/TO9A

(as performed and validated by Analytical Perspectives)

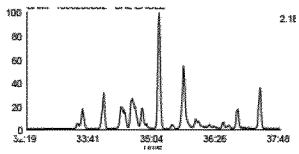
1. Described below are key aspects of the various improvements. For more information and details, refer to Analytical Perspectives Performance Commitment document, which includes QC Acceptance Criteria & Corrective Actions.

2. The reference Method 8290 requires a Soxhlet extraction with toluene for non-biological solid matrices. Our approach calls for the use of Soxhlet Dean-Stark (SDS) extraction with toluene. For biological tissues, hexane SDS extraction is used to prevent precipitation of lipids in the presence of water and methylene chloride. The SDS permits the progressive removal of the entire water contents from the sample matrix and, subsequently, from the extraction solvent system by way of an azeotrope formation between toluene (or when applicable, hexane) and water. During the extraction cycle, the water separates from the organic solvent inside the Dean-Stark arm. Pure organic solvent is now returning to the extraction vessel. The removal of the water from the extraction system ensures the sample matrix is extracted with pure toluene (or when applicable, hexane) rather than a mixture of organic solvent—water as it happens when Soxhlet alone is used. This modification results in a more effective extraction of the organics such as PCDD/Fs, which are more soluble in organic solvents than in water.

3. Our sample extract fractionation procedure is designed to remove a wide variety of interferences. Among the most common interferences, polychlorinated diphenylethers (PCDPEs), when present, can artificially elevate the concentrations of PCDFs. Our cleanup approach removes the bulk of the PCDPEs (or alleged PCDPEs) in air and air-related matrices (e.g., ash) so that their effect is reduced to less than 0.3 to 3 percent positive bias on the total PCDD/Fs. This estimate is based on a worst-case scenario whereby we assume the alleged PCDPE is solely responsible for the signal found in the PCDF channel. Over the years, the application of our cleanup procedures indicate that no PCDPEs are found in our sample extracts (see Fig. below showing an example of M23 data from a competitor lab where numerous PCDPEs constitute a major source of false positives). Our fractionation procedures for fish tissue are designed to eliminate PCDPEs that may interfere with the detection and analysis of PCDFs.



4. HpCDPEs in a M23 Sample as a major source of false positives from a competitor lab



5. OCDPEs in a M23 Sample as a major source of false positives from a competitor lab

6. To eliminate the risk of confusion between methods when referring to the various standards used throughout the procedures, the following nomenclature is applied:

    1. Extraction Standard (ES): Extraction standards are the seventeen 13C 12-labeled 2,3,7,8-substituted PCDD/F congeners, which are added to every sample before the extraction. They are used to monitor both the extraction and fractionation efficiencies as well as for quantitative and qualitative purposes. For air matrices, the ES is also used to compute the SS recoveries. Versions of the methods refer to them as "internal standards" or "labeled compounds".

    2. Cleanup Standard (CS) or Sampling Standards (SS): A group of five labeled PCDD/F congeners added to every sample immediately following the extraction and before the fractionation. They are representative of a number of homologue groups and are used to monitor the fractionation efficiencies.

    3. Alternate Standards (AS): 13C 12-1,3,6,8-TCDD and 13C 12-1,3,6,8-TCDF are used as additional cleanup standards to monitor for selective losses during the fractionation procedures, which can introduce a bias on totals as well as distort the congener profiles.

    4. Injection Standard (JS): Injection standards are a group of three labeled PCDD/F congeners, which are used for the preparation of the final extract for GC/MS analysis. Their function is to measure the recoveries of the ES and CS and to provide a means for insuring that the system's sensitivity performance remains acceptable. Versions of the methods referred to them as "recovery standards" or "labeled internal standards".

    5. Note that a similar system is adopted for PCBs, PAHs, and USVOAs.

7. The method calls for the use of nine (Method 8290) or 15 carbon-13 labeled Extraction standards (Method 1613) added to the sample before the extraction. Our fortification procedure consists in the addition of 17 carbon-13 labeled extraction standards to the sample before the extraction. One of the additional standards is 13C 12-OCDF, a compound that could not be used in the early eighties when Methods 8290/23/1613 were developed. Indeed, the available technology was unable to achieve chromatographic separation between OCDD and OCDF. From a mass spectrometry point of view, 13C 12-OCDF interferes with the measurement of OCDD and, is interfered by OCDD, especially when OCDD levels are high. With today's improved gas chromatographic column technology, the separation between the two congeners permits the introduction of such a valuable standard to monitor more specifically the recovery of OCDF and to measure more accurately the amounts of OCDF present in the sample. It is worth mentioning that the author of this document has verified, under certain laboratory lighting conditions, the light-induced thermal degradation of OCDF during the toluene Soxhlet extraction. Up to 80 –90 percent thermally-induced photodegradation of OCDF have been observed while none was found for OCDD under the exact same conditions. In the absence of 13C 12-OCDF, a significant negative bias would result for the measurement of OCDF if the corresponding labeled standard is not used.

8. Each of the methods' calibration curve is established with **five** individual solutions ranging in concentrations, for instance, from 0.5 pg/ m L to 100 pg/ m L for the TCDD/F. Our **seven-point** initial calibration curve's dynamic range extends two-fold lower (0.25 pg/ m L) and five-fold higher in concentration (500 pg/ m L). Furthermore, Methods 8290/1613/23/0023A minimum requirements for the acceptance of the initial calibration are RSDs ranging from 20-25 to 35 percent depending on the analyte. Our internal requirement calls for single digit RSDs. Higher precision and accuracy for the PCDD/Fs are the primary benefits of these modifications. Tables 1 and 2 summarize the two sets of ICAL used by Analytical Perspectives. The secondary ICAL—an option offered exclusively by Analytical Perspectives—is used for the analysis of samples containing high-level analytes requiring up to 20-fold dilutions. The secondary ICAL is a product under evaluation, and may not be used systematically until the benefits are fully established.

9. Methods 8290/23/1613/23/0023A do not address the absolute value for the analytes' RRFs. In order to ensure accurate measurements, Analytical Perspectives verifies that the RRF for specific analytes with an associated carbon-13 labeled extraction standard remains within a reasonable value from historical values (e.g., + 20 percent). The Laboratory Director can reject the ICal and request a new set of standard solutions to be prepared when such deviations are found with a new batch of standards. One critical aspect to successful analysis by isotope-dilution HRGC-HRMS is the reliability of the standards. To that effect, a number of verification procedures with stringent requirements are implemented and enforced (e.g., independent verification of the standards through the use of intra-source area ratios).

10. Methods 23/1613 verification of the initial calibration are conducted **only** at the beginning of every 12-H of operation during which samples are analyzed by HRGC/HRMS. Our procedures based on the BCS3 system require not only a front-end but also a **back-end** continuing calibration verification (concal). Additionally, according to our procedures, both front- and back-end verifications entail a verification of the ability to measure 2,3,7,8-TCDD **and** 2,3,7,8-TCDF in an isomer-specific mode and a verification of the various homologue groups retention time windows. This demonstration and verification is accomplished through the use of a new QA/QC sample concept known internally as the BCS3, which is part of our enfolded performance approach.

    1. The BCS3 is a QC sample used for true-stable isotope-dilution GC/MS methodologies to ensure the reliability and accuracy (precision and bias) of the determinations. It is prepared in stages at the same time as the batch of field samples; i.e., at each phase involving the addition of the ES, CS, JS to the samples. For air matrices, the BCS3 is initiated at the preparation stage of the sampling modules (i.e., XAD-2 resin or PUF) during which the SS are introduced inside the sorbent material. The BCS3 is analyzed at the beginning and at the end of a 12-H analytical sequence during which the associated samples are analyzed. In order to use the front- and back-end BCS3 averaged RRFs to process the samples, the individual front- and back-end RRFs need to meet a number of requirements as detailed in section 5.4 of this procedure..

    2. It is AP's policy to develop a database of sample projects where both the OPR and the BCS3 are analyzed for M1613 samples. Once the Laboratory Director has determined that such information has been obtained, then, any project completed under M1613 where an OPR is required will NOT have a BCS3. Only those projects not requiring an OPR will be processed and analyzed under the BCS3 system. Furthermore, when an OPR is required, only a CS3 – spiked with the usual isomeric interferences and the first and last eluters – will be analyzed at the beginning of the sequence. No ending CS3 will be done when OPR is required.

11. Methods 8290/1613/23/0023A injection standards is a mixture containing two carbon-13 labeled PCDD congeners. Our injection standards solution contains three carbon-13 labeled PCDD/F congeners.

12. The "initial demonstration of performance" is conducted annually while fortifying the sample with the unlabeled target analytes at our reporting limit (i.e., corresponding to the more challenging lowest calibration point of our curve). Precision and accuracy information is available from our Performance Commitment document.

13. For Method 1613 only: Until such a time when the BCS3 can be considered and approved by the Office of Water as a substitute for an on-going precision and accuracy, an OPR quality control sample is prepared with each extraction batch. No OPR is prepared for Method 8290, however. The BCS3 fulfills a more valuable function than the OPR.

14. Our data acquisition and validation procedures require the monitoring and assessment of "quantitative interferences". When present, specific corrective actions may be necessary when they adversely impact the quality of the data. It is our policy to deliver data of quality; a policy that often results in carrying out additional (and outside the scope of the methods) fractionation procedures for complex samples.

15. Reporting of data is accomplished using a format that is accessible to a wide range of Users. It is designed to minimize the need for our clients to perform additional interpretation of the laboratory data. A three-part set of sample summary results is provided in an electronic format (Excel). Our CLP-like data package comes in both hardcopy and CD versions. The latter is integrated and interactive.

16. A correction for the contribution at m/z 322 from the CS (37Cl 4-2,3,7,8-TCDD) is applied automatically in our calculations.

17. Analytes found at a concentration below 1/10 th our reporting limit are reported as ND with a detection limit equals to 01 xRL.

18. Analytes whose ion-abundance ratio is outside the method's limits are reported as EMPC – estimated maximum possible concentration; a concept introduced in the early eighties during the development of the first version of USEPA Method 8290. An EMPC is triggered whenever one particular identification criterion for PCDD/Fs is not met. Its value, particularly in risk assessment studies, is found in circumstances when specific analytical factors can lead to possible false negatives. Understanding the analytical factors prompting an EMPC plays an important part in the formulation of effective course of actions or in the development of a strategy for reporting data.We also recognize the different – and sometimes conflicting – realities and needs of the ultimate users; i.e., the regulators, the risk assessors, and the regulated communities. When acquiring data by high-resolution GC/MS, the mass spectrometer is operating in the selected ion-monitoring mode. For each compound of interest, the mass spectrometer records the response of two characteristic ions from the molecular ion cluster. The ion-abundance ratio between the two characteristic ions must fall within accepted ranges for the peak to be identified as a PCDD/F congener. Should the ion-abundance ratio fall outside the permissible range, the corresponding GC peak cannot be identified as a PCDD/F congener. However, if the ratio error is assumed to be due to a contributing interference to one of the ions, then an EMPC may be derived from the unaffected ion and the natural abundance ratio. In essence, one performs a "mathematical" operation removing the "contribution" of the interference, if the latter is the primary reason for triggering the EMPC reporting.

    It is true that a co-eluting chemical interference can cause the ion-abundance ratio to exceed the method's limits (e.g., the impurity in the commercially available 37Cl 4-2,3,7,8-TCDD). However, for practical purposes, and before rushing into the so-called "confirmation" analyses and/or additional cleanups, which may in some cases amount to unethical practices, it helps to appreciate the fact that over 99 percent of the time, the EMPC is triggered by "ion statistics" and not by a chemical interference.

    Indeed, the uncertainty associated with the measurement of an ion-abundance ratio of two "weak" signals is equal to the sum of the variances associated with the individual signals. The weaker the S/N is, the larger the uncertainty of the measurement is. Ratio ing two numbers with large variances can result in the ion-abundance ratio to easily exceed the +15 percent window. In such case, a "confirmation" analysis is pointless unless the S/N is significantly improved. Our methodology reports EMPCs as such. Whenever a chemical interference can be discerned, we comment in the narrative on the potential impact on the data, or what actions have been taken or attempted to improve the specificity or to remove the interference, or its effect.

    For circumstances whereby an EMPC cannot be reported, we report any out-of-ratio criterion peak eluting at the retention time of a 2,3,7,8-substituted congener as an ND using the peak concentration as the detection limit.

3 Appendix

Tables 6, 6A, 7, 7A of M1613B
(as requested by SCDHEC)

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3–12.9	6.7–15.8	7.8–12.9
2,3,7,8-TCDF	10	2.0	8.7–13.7	7.5–15.8	8.4–12.0
1,2,3,7,8-PeCDD	50	7.5	38–66	35–71	39–65
1,2,3,7,8-PeCDF	50	7.5	43–62	40–67	41–60
2,3,4,7,8-PeCDF	50	8.6	36–75	34–80	41–61
1,2,3,4,7,8-HxCDD	50	9.4	39–76	35–82	39–64
1,2,3,6,7,8-HxCDD	50	7.7	42–62	38–67	39–64
1,2,3,7,8,9-HxCDD	50	11.1	37–71	32–81	41–61
1,2,3,4,7,8-HxCDF	50	8.7	41–59	36–67	45–56
1,2,3,6,7,8-HxCDF	50	6.7	46–60	42–65	44–57
1,2,3,7,8,9-HxCDF	50	6.4	42–61	39–65	45–56
2,3,4,6,7,8-HxCDF	50	7.4	37–74	35–78	44–57
1,2,3,4,6,7,8-HpCDD	50	7.7	38–65	35–70	43–58
1,2,3,4,6,7,8-HpCDF	50	6.3	45–56	41–61	45–55
1,2,3,4,7,8,9-HpCDF	50	8.1	43–63	39–69	43–58
OCDD	100	19	89–127	78–144	79–126
OCDF	100	27	74–146	63–170	63–159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28–134	20–175	82–121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31–113	22–152	71–140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27–184	21–227	62–160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27–156	21–192	76–130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16–279	13–328	77–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29–147	21–193	85–117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34–122	25–163	85–118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27–152	19–202	76–131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30–122	21–159	70–143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24–157	17–205	74–135
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	37	29–136	22–176	73–137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34–129	26–166	72–138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32–110	21–158	78–129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28–141	20–186	77–129
$^{13}C_{12}$-OCDD	200	95	41–276	26–397	96–415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9–15.4	3.1–19.1	7.9–12.7

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 6A. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ONLY TETRA COMPOUNDS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] s (ng/mL)	IPR [2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7–12.4	7.3–14.6	8.2–12.3
2,3,7,8-TCDF	10	2.0	9.1–13.1	8.0–14.7	8.6–11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32–115	25–141	85–117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35–99	26–126	76–131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5–13.4	3.7–15.8	8.3–12.1

[1] All specifications are given as concentration in the final extract, assuming a 20 µL volume.
[2] s = standard deviation of the concentration.
[3] X = average concentration.

TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL) [1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25–164	25–164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24–169	24–169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25–181	25–181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24–185	24–185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21–178	21–178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32–141	32–141
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	28–130	28–130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26–152	26–152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26–123	26–123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29–147	29–147
$^{13}C_{12}$-2,3,4,6,7,8,-HxCDF	100	28–136	28–136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23–140	23–140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28–143	28–143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26–138	26–138
$^{13}C_{12}$-OCDD	200	34–313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5–19.7	35-197

[1] Specification given as concentration in the final extract, assuming a 20-µL volume.

TABLE 7A. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ONLY TETRA COMPOUNDS ARE TESTED

Compound	Test Conc. (ng/mL)	Labeled compound recovery (ng/mL) [1]	Labeled compound recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2–16.4	42–164

[1] Specification given as concentration in the final extract, assuming a 20 µL volume.

List of Abbreviations &Acronyms

1. AS = alternate standard
2. A_x = target analyte
3. BCS_3 = batch control spike
4. CAA = Clean Air Act
5. COC = chain of custody
6. CPSM = column performance standard mixture
7. CS_3 = calibration solution corresponding to the middle point of the initial calibration curve
8. CS = cleanup standard
9. CWA = Clean Water Act
10. *dfa* Technology = dioxin-furan array (fingerprinting reminiscent of DNA plates)
11. DOC = documentation of capability
12. DUP = duplicate
13. EDL = estimated detection limit (sample- and analyte-specific)
14. ES = extraction standard (isotopically labeled standard added before the extraction)
15. GC = gas chromatography
16. ICAL = initial calibration
17. ID-HRMS = comprehensive and stable isotope-dilution high-resolution mass spectrometry
18. Ind. Val. = independent validation
19. JS = injection standard
20. LOD = limit of detection
21. LOQ = limit of quantitation
22. MB = lab method blank
23. MDL = method detection limit (not sample-specific)
24. M/ΔM = mass spectrometer resolving power
25. MIR = Methods Innovation Rule
26. ML = minimum level (equivalent to lowest point on the calibration curve)
27. MS/MSD = matrix spike/matrix spike duplicate
28. ND = not detected
29. NELAC = National Environmental Laboratory Accreditation Conference
30. OPR = on-going precision & recovery (equivalent to LCS or Lab Control Spike)
31. PAH = polynuclear aromatic hydrocarbon
32. PBMS = performance-based measurement system
33. PCB = polychlorinated biphenyl
34. PCDD/F = polychlorinated dibenzo-*p*-dioxin and dibenzofuran
35. PD = percent difference
36. PE = performance evaluation sample
37. QI = quantitative interference
38. QuanTIC = selected SVOAs by full-scan GC/MS (ID-HRMS)
39. RCRA = Resources Recovery Act
40. RL = reporting limit (usually represents the lowest point on the calibration curve or ML)
41. RPD = relative percent difference
42. RRF = relative response factor
43. RSD = relative standard deviation
44. RTW = retention time defining window solution
45. SDWA = Safe Drinking Water Act
46. SICP = selected ion current profile
47. S/N = signal-to-noise ratio
48. SRM = standard reference material
49. SS = sampling standard
50. TEQ = toxic equivalency quotient
51. TSCA = Toxic Substances Control Act
52. U-SVOA = ultra-semi volatile analyte (selected SVOAs by SIR by ID-HRMS)
53. VER = continuing calibration verification (equivalent to ConCal)
54. WHO-2 / WHO-2S = ID-HRMS assay for the 29 World Health Organization target analytes (S = serum)

SOP No. AP-CM-13	Revision: 1	Effective: 22 MAY 12	Supercedes: N/A
DF HIGH VOLUME SAMPLING ADDENDUM **USEPA METHODs 8290, 1613, 23, 0023A & TO-9A**			
Author: Julie Martin			
Management – Bryan Vining, Ph.D.		22 MAY 12	
QA Officer - Bryan Vining, Ph.D.		22 MAY 12	

Unless otherwise listed here, these samples shall be processed and analyzed according to the procedures and methods stated in the appropriate Analytical Perspectives SOPs. This procedure augments SOP AP-CM-5, Revision 15.

New spiking solutions as well as new terms were created for this procedure.

This procedure creates multi-component samples analogous to air samples; the extraction of these samples follows the same air extraction procedures used when no split or archive is required (See section 14.1.8 of SOP AP-CM-5, Revision 15.

The following text and tables augment section 19 of SOP AP-CM-5, Revision 15.

RECOVERY LIMITS:

RECOVERY LIMITS FOR THE DIOXIN/FURAN DS_{FS} AND SS SPIKES

Spiking Solution	% Recovery
DS_{FS} spike (MeOH)	40% - 130%
SS spike	70% - 130%

The following text and tables augment section 23 of SOP AP-CM-5, Revision 15.

DYNAMIC STANDARD (DS_{FS}): A SPIKE USED IN THE FIELD TO DETERMINE HOW WELL THE HVS PROCEDURE RECOVERS SPECIFIC ANALYTES DURING THE SAMPLING PROCESS. METHANOL IS USED AS THE CARRIER SOLVENT.

DIOXIN/FURAN DS_{FS} SPIKE SOLUTION CONSTITUENTS

Compound	Dynamic Spike Standards Amount Spiked ng
$^{13}C_{12}$-1,2,7,8-TCDD	2
$^{13}C_{12}$-1,2,4,7,8-PeCDD	2
$^{13}C_{12}$-1,2,3,4,6,8-HxCDD	2
$^{13}C_{12}$-1,2,3,4,6,7,9-HpCDD	2
$^{13}C_{12}$-1,3,7,8-TCDD	2

STATIC STANDARD (SS): IDENTICAL IN COMPOSITION TO THE SAMPLING STANDARD USED FOR OTHER PROCEDURES. THE SS IS SPIKED INTO THE SORBENT PRIOR TO SAMPLING. IN THE HVS PROCEDURE THE CS/SS SPIKE IS USED ONLY AS A SAMPLING STANDARD AND NOT AS A CLEANUP STANDARD.

DIOXIN/FURAN SS SOLUTION CONSTITUENTS

Compound	Static Spike Standards Amount Spiked (ng)
$^{37}Cl_4$-2,3,7,8-TCDD	0.8
$^{13}C_{12}$-1,2,3,4,7-PeCDD	2
$^{13}C_{12}$-1,2,3,4,6-PeCDF	2
$^{13}C_{12}$-1,2,3,4,6,9-HxCDF	2
$^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF	2

ALTERNATE CLEANUP STANDARD (AS): THE USUAL AS STANDARD USED FOR DIOXIN/FURAN PROJECTS. THE CS/SS STANDARD IS NOT USED AS A CLEANUP STANDARD FOR THE HVS PROCEDURE.

DIOXIN/FURAN AS SOLUTION CONSTITUENTS

Compound	Alternate Cleanup Standard Amount Spiked ng
$^{13}C_{12}$-1,3,6,8-TCDD	2
$^{13}C_{12}$-1,3,6,8-TCDF	2

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AP-CM-7	Revision: 9-1	Effective: 08 OCT 10	Replaces: 26 AUG 10
HIGH RESOLUTION MASS SPECTROMETRY ***METHOD 1668A for Solid/Air/Aqueous/Tissue Matrices***			
Author: Yves Tondeur, Ph.D.			
Management – Yves Tondeur Date 26 AUG 10			
QA Officer – Bryan Vining, Ph.D. Date 26 AUG 10			

1. PURPOSE/IDENTIFICATION

    1. **This procedure describes the analytical techniques used for extraction and analysis of aqueous, solid, oil, wipe, waste, air and tissue samples for polychlorinated biphenyls (PCBs) by EPA Method 1668B.**

2. APPLICABLE MATRICES

    1. This method is applicable to all matrices.

3. DETECTION LIMIT

    1. The limits of detection and quantitation in various matrices are available in the Performance Commitment document.

4. SCOPE AND APPLICATION

    1. This method is for the determination of coplanar polychlorinated biphenyls (PCBs), mono-ortho substituted PCB congeners, the 10 PCB homologue groups as well as the 209 PCB congeners at the quantitation limits listed in Table 1 for water, soil, sediment, sludge, ash, tissue, and other sample matrices such as air by gas chromatography/high-resolution mass spectrometry/selective ion monitoring (GC/HRMS/SIM). The method is based upon the combined features of EPA Method 1668B to extract, cleanup sample extracts, and measure toxic PCB congener target compounds.

    2. Twenty-seven $^{13}C_{12}$-PCB congeners, including the 12 WHO congeners, are added to each sample as Extraction Standards. Following a matrix-specific extraction, the extracts are fortified with a group of three $^{13}C_{12}$-PCB congeners as Cleanup Standards. Once cleaned up, the residue is fortified with a mixture of five $^{13}C_{12}$-PCB congeners as Injection Standards. For air samples, the role of the CS is modified so that they can be used as Sampling Standards; i.e., they are added to the sampling module before the sampling session. A five-point ICAL is used to derived the analytes and labeled compounds RRFs. For assays requiring an OPR, a front-end CS3 is analyzed while the BCS_3 system – developed for Method 8290B – is applied for assays not mandating an OPR (e.g., air samples, R&D, SW…)..

5. SUMMARY OF THE TEST METHOD

AQUEOUS SAMPLES (<1% solids) - Stable isotopically labeled analogs of PCB target congeners are spiked into a one-liter sample and either vacuum-filtered (if particulates are present) through a glass-fiber filter, toluene-SDS the filter and liquid-liquid extract the filtrate with methylene chloride. If the sample does not show visible particulates, a liquid-liquid partitioning is carried out with methylene chloride.

2. SOLID, SEMI-SOLID, AND MULTI-PHASE SAMPLES (except tissue) - The labeled compounds are spiked into the sample containing 10 g dry-weight equivalent. Samples containing multiple phases are filtered and any aqueous liquid discarded. Coarse solids are ground or homogenized. Any non-aqueous liquid from multi-phase samples is combined with the solids and extracted in a Soxhlet/Dean Stark (SDS) extractor. The extract is concentrated for cleanup. Results are reported on a dry-weight basis.
3. FISH AND TISSUE- A 25-g aliquot of sample is homogenized, and spiked with the labeled isotope compounds. The sample is mixed with Hydromatrix™ and extracted for 16 hours using hexane in a Soxhlet Dean-Stark extractor over acid-coated silica gel (see Method 8290 for tissue for details). The extract is evaporated to dryness. The lipid content is determined using a separate aliquot of the tissue as per the procedure described for Method 8290.
4. AIR SAMPLES – For Modified Method Five and ambient air samples, the sampling sorbent is fortified with a mixture of Sampling Standards before sampling. Upon return to the laboratory, the various components of the train are processed as per the M23 diagram (see Method 23). The extraction starts with hexane SDS for 16 hours followed by toluene for 16 hours. This approach is applicable to PCBs whether in conjunction with PCDD/Fs or not, whether in conjunction with PAHs or not, and whether selected PCB congeners are assayed or not. The combination of solvent is necessary to ensure the recovery of low- and high-molecular weight congeners as well as coplanar and mono-ortho congeners. Alternatively, it is permitted to perform an 8-H hexane SDS followed by an 8-H toluene SDS.
5. The extract is fortified with Cleanup Standards and fractionated using the ASECS procedure (see Method 8290 or Fractionation SOP). For air samples, do not add the CS because the Cleanup Standards are actually playing the role of Sampling Standards and were introduced inside the sampling module before the sampling session. Collect the PCB fraction. After cleanup, the extract is concentrated to near dryness. Injection Standards are added to each extract and an aliquot of the extract is injected. The analytes are separated by the GC and detected by gas chromatography/high resolution mass spectrometry/selective ion monitoring (GC/HRMS/SIM) to achieve the required quantitation limits of the method. Two exact m/z's are monitored for each homologue.
    A. For the measurement of the 209 PCB congeners, the GC/MS system is calibrated using the native and labeled PCB congeners listed in Table 1.
6. An individual PCB congener is identified by comparing the GC retention time and ion abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical ion-abundance ratio of the two exact m/z's. Isomer specificity for the toxic PCBs is achieved using GC columns that resolve these congeners from the other PCBs. For this SOP, the SB Octyl 30-m column is used as described in Method 1668B. A 60-m DB-5MS is also used for WHO 29 target analytes where the SB-Octyl co-eluting pair of iso-TEF isomers PCB-156/157 can be resolved. Data validating such isomer-specificity were supplied to NELAC by comparing the analyses of a mixture containing all 209 congeners for the two co-eluting isomers on the SB-Octyl column and the DB-5MS column (click here for details).
7. Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of two ways:

    1. For PCB congeners with labeled analogs, the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.
    2. For PCB congeners without labeled isotopes, and for PCB homologues, the GC/MS system shall be calibrated and the concentration of each compound determined using internal standard technique.
    3. Note that different relationships are used as permitted by the method (Table 3). The selection is based on the rationale discussed in the attachment, which can be viewed by clicking here.
    4. The effects from quantitative interferences, a common occurrence observed with PCB analyses targeting such a wide range of compounds, are mitigated by the use of a custom-developed and validated program known under the name of "Equalizer". The program is considered intellectual property and no written details will be provided until a peer-reviewed publication of the concept and the demonstration of its benefits for this type of assays is completed. The concept is also considered proprietary, and we request any third parties made aware of this unique, innovative and powerful tool to respect the confidential aspects until the paper is accepted for publication. The raw data shows the file name appended with the letters "EQ" to indicate that the data underwent the

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special treatment with the ©Equalizer.

5. For dichlorinated congeners, a single ion corresponding to the $M^{+\cdot}$ is used for the quantitations and to determine S/N. Indeed, the M+2 ion is interfered by background ions originating from the reference compound PFK. The latter increases the chemical noise and leads to unrealistically high detection limits. The letters "SI" appear on the raw data to indicate when such feature is turned on at the data generation stage. Retention time matching, detection of the molecular ion and other aspects associated with the number of possible dichlorinated congeners are considered sufficient to provide reliable data.

8. The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems. Under the BCS_3 system, such performance assessment can be obtained. However, under the OPR system, we cannot make the same statement.

6. DEFINITIONS

1. Definitions (and more thorough explanations) of concepts introduced by Analytical Perspectives may be found in the Performance Commitment document.

7. INTERFERENCES

1. All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks with each sample batch. Note that with PCBs, background contributions are very common in a laboratory environment. Method 1668B introduced the EML concept in recognition of this fact. However, AP has adopted a policy to "beat" these EMLs as much as possible by investigating the sources of PCB background contributions and ultimately achieve the same results as currently achieved with PCDD/Fs (i.e., no detectable signals). This effort might take some time to achieve. EMLs constitute a "nice" protection that should not take away our determination to succeed in this endeavor.

    1. The reference matrix should simulate, as closely as possible, the sample matrix under test. For IPAs/OPRs, reagent water can be used to simulate water samples; playground sand or white quartz sand can be used to simulate soils; filter paper can be used to simulate papers or similar materials; and corn oil or cod fish can be used to simulate tissues. However, for Method Blanks, use only the materials that are part of the field samples processing. For instance, if Hydromatrix™ is used to prepare a serum sample, than, the same amount of Hydromatrix™ from the same lot number should be used for the Method Blank. Adding to the MB some oil, which is not added to the field samples, is an action that ignores the purpose and function of the MB.

2. Interferences co-extracted from samples will vary from source to source, depending on the site being sampled. The cleanup steps can be used to reduce or eliminate such interferences. It is worth mentioning that assaying for such a broad range of target compounds, complications will results. Indeed, certain types of interferences (a.k.a. quantitative interferences, QI) cannot be removed without removing the target analytes. Appropriate actions will be taken and considered on a case-by-case basis. These can range from additional cleanup, dilutions, to using the ©Equalizer and the application of adequate data qualifiers and interpretation/discussion in the case narrative.

8. SAFETY

1. Standard sample preparation laboratory safety precautions apply, as outlined in AP's Health and Safety SOPs.

9. EQUIPMENT AND SUPPLIES

1. CTC Autosampler
2. PC with MassLynx
3. Water Cooler.
4. Magnetic Sector High Resolution Mass Spectrometer
5. Food Slicer.
6. Pipets, disposable, serological, 10 mL.
7. Pipets, Pasteur.
8. Amber glass bottles, 1 liter (Teflon-lined screw cap).
9. Two-liter separatory funnels.
10. Teflon boiling chips.
11. glass chromatographic column (see ASECS in Method 8290)
12. N-Evaporator
13. Conical vials, 2 mL.
14. Pyrex fiber glass, 8µm sliver (glass wool plug).
15. Funnels, 100 mL.
16. Dean-Stark Trap, condenser and flask.
19. Rotary Evaporator.
20. Round-bottom flasks, 500 mL.
21. Top-Loader Balance.
22. Injection vials.
23. Electrothermal electromantles.
24. Drying oven.
25. Whatman glass microfibre filters
26. HP 6890 Gas Chromatograph

10. REAGENTS, STANDARDS AND SOLVENTS

1. Reagents

    1. Sulfuric acid, concentrated.

    2. Silica gel. Highest purity grade.

    3. Sodium Thiosulfate, 80 mg/L

    4. Water, distilled.

    5. Florisil.

    6. Prepurified nitrogen gas.

    7. Anhydrous sodium sulfate.

2. Solvents

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1. Methylene chloride. Highest available purity.
2. Hexane. Highest available purity.
3. Tetradecane. Highest available purity.
4. Toluene. Highest available purity.
5. Methanol. Highest available purity.

3. Standards

1. PCB Analytical standards (Cambridge Isotope Laboratory, Wooburn, MA).
2. For details on the preparation and independent verification, see Standards SOP in the Preparation of Supplies Section.
3. The NS (native spike) solution used for the BCS_3 must originate from an independent source

11. COLLECTION, PRESERVATION, AND HANDLING

1. Aqueous Samples

1. At minimum, collect one liter of sample. If residual chlorine is present, add 80mg/L of sodium thiosulfate.
2. Adjust sample pH 2-3 with sulfuric acid.
3. Store aqueous samples in the dark at 2-6°C.

2. Solid Samples

1. Solid samples are collected as grab samples using wide-mouth jars.
2. Store solid, semi-solid, oily, and mixed-phase samples in the dark at 2-6°C.

3. Fish and Tissue Samples

1. Fish may be cleaned, filleted, or processed in other ways such that the sample is received as whole fish, fish fillets or other tissues for analysis.
2. Samples must be frozen and maintained in the dark at <-18-20°C.

4. Holding Times

1. If stored in the dark at 2-6°C and preserved as described in Section 7.3, aqueous samples may be stored for up to one year.
2. If stored in the dark at <-10°C, solid, semi-solid, oily, multi-phase, fish and tissue samples may be stored for up to one year. If stored at 2-4°C, the holding time for the extraction becomes 30 days from collection.
3. Sample extracts should be stored at 4°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

12. QUALITY CONTROL

Quality control is demonstrated by an initial demonstration of laboratory capability, analysis of spiked samples with labeled compounds to evaluate and document data quality, and the analyses of standards and blanks as a test of continued performance.

1, Initial Precision and Recovery (IPA): Four aliquots of the diluted precision and recovery standard are analyzed to establish the ability to generate acceptable precision and accuracy in reference matrix. Alternatively, AP's initial demonstration is performed while conducting the MDL studies using a spike level that is 20 times lower than what the method's calls for. Recently, AP has adopted a policy to use a mixture containing the 209 congeners for IPAs and future MDLs.
   1. An IPA is performed prior to the first time this method is used and any time the method or instrumentation is modified.
   2. Using the results of the set of four analyses, calculate the average concentration (x) and the standard deviation (s) for each compound.
   3. Compare x and s for each native and labeled compound with the limits for IPA in Table 6 of method 1668B. If any individual s exceeds the precision limit or any individual x fall outside the range for accuracy, the test must be repeated. For congeners that are not listed in the method table, refer to the limits posted in the spreadsheet summarizing the data.
2. Method Blank (MB): Method Blank is a sand, distilled water or other appropriate matrix preparation that is free from native analyte that has been prepared and analyzed using the same procedures followed for the rest of the sample batch.
   1. A MB is run with every analytical batch or 20 samples, whichever is less, per matrix type.
   2. Analytical data is accepted (with a data qualifier) if the amount found in the MB is less than one tenth of the level found in the associated samples. Otherwise, the samples are re-extracted and analyzed. Use the EMLs in Method 1668B for guidance only. Use the "B" data qualifier when a specific congener is found at a level above the RL or when at a level that is not "significantly" different then the one found in the field sample even if below the RL.
3. Ongoing Precision and Recovery (OPR): An ongoing precision and recovery sample is prepared by adding a known quantity of native standard to an interferant-free matrix and used to assess method performance (precision and recovery).
   1. Spike the native compounds into the sample at a level corresponding to the CS3.
   2. An OPR is analyzed with every analytical batch or 20 samples (whichever is less) per matrix type.
   3. For each native and labeled compound, compare the concentration with the limits for ongoing accuracy in Table 6 in Method 1668B.
4. Matrix Spike (MS/MSD): A matrix spike sample is prepared by adding a known quantity of native standard to a sample matrix prior to extraction. The MS/MSD are only prepared when requested by the clientele. Although, it is customarily to use only the unlabeled compounds present in the ICAL, AAP might consider using the 209 congeners once every other year to assess its ability to determine the full list of congeners.
   1. Spike the native compounds into the sample at a level corresponding to the CS3.
   2. The relative percent difference between MS/MSD samples should be ≤50%.
5 Batch CS_3: For air samples and other sample projects not requiring an OPR and/or MS/MSD, a Batch CS_3 is prepared and analyzed at the beginning and at the end of each 12-H analytical sequence according to the descriptions provided in Method 8290. The concentrations of the Batch CS_3 are the same as the CS_3 of the ICAL. As indicated earlier, a database of Batch CS_3's will become the basis for developing control limits. Until such time, the control limits currently proposed for Method 8290 will be considered. For more details on the BCS_3 concept, refer to the Performance Commitment document.
6 Solvent Blank Spike (SBS): To ensure that no carry-overs are operating, an SBS injection is performed right after the analysis of the BCS_3 (or CS3, or OPR). The goal is to verify that no peaks from the previous run are found with a S/N>2.5. However, in order to distinguish the absence of carry-overs from a "miss-injection", the SBS is used instead of just nonane by itself. The SBS contains a number of PCB congeners ranging from Cl_3 to Cl_7 (see list below). A second function fulfilled by the SBS is verification of the overall instrument sensitivity. The various PCB congeners present in the SBS are present at a concentration that is ½ the lowest point on the calibration curve (or ML; 0.5 pg/µL).

PCB Congeners in the SBS	
Tri-CB:	36
TCB:	72, 79, 78
PeCB:	96, 98, 89, 108, 106

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HxCB: 152, 166
HpCB: 184, 182
OCB: 204

13. CALIBRATION AND STANDARDIZATION

1. Initial Calibration
   1. Inject the reference compound perfluorokerosene (PFK). PFK provides the required lock masses and is used for tuning the mass spectrometer.
   2. Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000. For each mass descriptor, monitor and record the resolution and exact m/z of three to five reference peaks covering the range of the descriptor.
   3. An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ± 220% throughout the respective retention time window.
   4. For the measurement of PCBs, the exact m/z's to be monitored in each descriptor are listed in Table 6 of the method.
   5. Inject 1 µL of the Window Defining Mix (CPSM) or Batch CS_3.
      1. The first and last eluters are verified to be within the appropriate retention time windows for each chlorination level.
   6. Under the same conditions, inject 1 µLL of each of the five calibration solutions containing all PCB isomers. Calibration standard solutions are presented in Table 2.
      1. The signal to noise ratio (S/N) must exceed 10:1 for all ions monitored,
      2. The ion abundance ratio measurements must be within ± 15% of the theoretical ratio.
   7. Calibration by Isotope Dilution: Isotope dilution calibration is used for the native PCBs for which labeled compounds are added to samples prior to extraction.
      1. If the relative response for any compound is less than 20% coefficient of variation over the 5 point calibration range, an averaged relative response is used for that compound; otherwise, the complete calibration curve for that compound is used over the 5 point range.
   8. Calibration by Internal Standard: Internal standard method is used for the determination of native PCBs for which a labeled compound is not available.
      1. If the response factor for any compound is less than 35% coefficient of variation over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

2. Continuing Calibration

   1. Follow the BCS_3 requirements. Using the same operating conditions as established for the ICAL, inject 1 mL of the batch control spike (BCS_3)) at the beginning and end of each 12-hour period during which samples are analyzed in order to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, to establish the PCB retention time windows and isomer-specificities, and to validate the standards and the spiking technique. When true 1668 requirements are required, follow the procedures below.

   2. Inject a column performance standard mix (CPSM) to verify retention time windows.

      1. The first and last PCB eluters are verified to be within the homologue retention time windows.

   3. Inject a mid-range standard from the initial calibration curve (CS3) at the beginning and end of every 12 hours. The following criteria must be met:

      1. The relative response factors for the mid-range standard are within the limits established in Method 1668. That is, the percent RSD for the mean response factors must be within the method's tolerances.

      2. The ion ratios are within 15 percent of the theoretical.

      3. The signal to noise ratio (S/N) exceeds 10:1 for all ions monitored.

      4. The retention times must be within the criteria established in Method 1668..

14. EXTRACTION AND CLEANUP PROCEDURES

1. Extraction
   1. Determine the percent solids on all samples. Weigh 2-10g of sample, dry overnight in 110°C oven and re-weigh.
   2. AQUEOUS OR SAMPLES WITH <1% SOLIDS: Extract sample using one of the following two extraction procedures:
      Using 1 L of the sample, spike 2 ng of the Extraction Standards into the sample. Into the OPR, spike the native compounds at a level consistent with the CS3 concentration. If particulates are present, filter (0.45 µm) and perform a dual extraction (liq-liq with MC on the filtrate and toluene SDS on the filter/solid). SDS Soxhlet extract the filter with toluene for 16 hours. Combine the extracts and solvent exchange into hexane. Proceed with cleanup procedures. In the absence of particulates, liquid-liquid partition with MC (3x60 mL in separatory funnel or using the CLL). Allow the organic layer to separate and collect by passing through a funnel with cleaned Na_2SO_4 into a 500mL round bottom. Concentrate and solvent-exchange into hexane.
      Proceed with appropriate cleanup procedures.
   3. SOIL, SEDIMENT, SLUDGE OR SAMPLES WITH >1% SOLIDS: Spike 2 ng of the Extraction Standards into the thimble containing 10-20 g equivalent dry weight of sample mixed with Hydromatrix™ .. SDS Soxhlet extract for 16 hours hexane followed by 16 H with toluene. Concentrate, combine and solvent-exchange into hexane. Proceed with cleanup procedures. It is permitted to perform an 8-H hexane SDS followed by an 8-H toluene SDS extraction.
   4. MULTI-PHASE SAMPLES: Using the percent solids, determine the volume of sample that will provide 10-20 g of solids, up to 1L of sample. Pressure filter the amount of sample determined through glass-fiber filter paper. If necessary, separate the phases and/or settle the solids, centrifuge the aliquots before filtration. Discard any aqueous phase, if present. Remove any non-aqueous liquid present and reserve the maximum amount filtered from the sample or 10 g, whichever is less, for combination with the solid phase.
   5. ASH SAMPLES: Spike 2 ng of the Extraction Standards into the thimble containing 5 g of sample mixed with Hydromatrix™.. SDS Soxhlet extract for 16 hours with hexane, followed by 16 H with toluene. Concentrate, combine and solvent-exchange into hexane. Proceed with cleanup procedures. For ash matrices, do not use the two 8-H SDS extraction option.
   6. AIR SAMPLES: See Methods 23/8290B for procedural details. Depending on whether or not PCBs are analyzed in conjunction with PCDD/Fs and/or PAHs, the spike amount ranges from 2 ng to 4 ng. Custom-made charts are used to help with the description of the spike profiles, the sample handling and extractions. Because these charts are designed on a per project basis, see the project folder for the charts. The resin/PUF sorbents are pre-spiked with three Sampling Standards (i.e., the CS in 1668B).
   7. FISH AND TISSUE SAMPLES: Mix 25 g of well ground fish with Hydromatrix™.. Stir frequently to remove any lumps. Transfer the mixture to a thimble containing 50 g of acid-coated silica gel. Spike 2 ng of the Extraction Standards. Soxhlet extract for 16 hours with hexane. Proceed with cleanup procedures. Calculate the % lipids on a separate aliquot.
   8. % Lipids
   1. Using a 5-to-10-g separate aliquot, extract inside a VOA vial using MC and sonication.
   2. Filter through a glasswool plug containing sodium sulfate.
   3. Allow the extract to air dry completely and then place in a vacuum oven overnight at room temperature.
   4. Weigh the residue on the balance and record the weight. Calculate the % lipids using the following equation:
      1. % lipids = $\frac{\text{lipid residue wt.}}{\text{sample wt.}} \times 100$

2. Cleanups **(note: refer to specific SOPs for the latest version; this Core Method SOP may not contain the same level of details)**.

    1. If not done, add the Cleanup Standards. Rotovap to C_{14}. Proceed to first cleanup.

    2. ABP-Acid/base partitioning ("dirty" samples only)

        1. Acid/Base Silica Column (see SOP AP-SP-CU1 current revision)

        2. Florisil Column (see SOP AP-SP-CU1 current revision)

3. GC/MS ANALYSIS

    1. Establish the necessary operating conditions. The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, OPR aliquots, BCS_3 and samples. Use the SB-Octyl GC column described in Method 1668B. For isomer specific determination of the PCB-156 and PCB-157, use the WHO 2 SOP.
    2. The reference perfluorokerosene (PFK) provides the required lock masses and is used for tuning the mass spectrometer.
        1. An appropriate lock mass will be monitored for each descriptor and shall not vary by more than ± 20% throughout the respective retention time window.
        2. Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000. For each descriptor, monitor and record the resolution and exact m/z of three to five reference peaks covering the range of the descriptor. The mass resolution check is achieved before any analysis is performed and at the end of each 12-hour shift.
    3. Set up the analytical run following this sequential injection pattern: Window Defining Mix or CPSM, CS3, OPR, BCS_3, Solvent Blank, Method Blank, Samples, closing BCS_3. Note that under the BCS_3 system, no CS3 or OPR are required. And similarly, under the OPR system, no BCS_3 are required. However, it is important to emphasize that AP has been operating in dual mode for many months before adopting this policy.
    4. Inject 1µL of the Window Defining Mix.
        1. The first and last eluters are verified to be within the appropriate retention time windows for each chlorination level.
    5. Inject either a mid-range standard from the initial calibration curve (CS3), or a BCS_3 created for the samples to be analyzed. The following criteria must be met:
        1. Calculate the concentration of each native compound either by isotope dilution or internal standard technique. Each compound must be within the verification limits established in Method 1668B.
        2. The ion ratios must be within 15% of theoretical.
        3. The signal to noise ratio (s/n) must exceed 10:1 for all ions monitored.
        4. Criteria for BCS_3 are available from M8290B SOP (i.e., in addition to the RT, S/N, ion-abundance ratio, a PD of $\leq$20 percent for Ax, PD$\leq$50 percent for ES/CS/SS; RPD $\leq$10 percent for Ax; RPD $\leq$20 percent for ES/CS/SS).
    6. Qualitative Determination
        1. To identify a chromatographic peak as a PCB (either an unlabeled or a labeled compound). It must meet the following criteria:
            1. The signals for the two exact m/z being monitored must be present and must maximize within ±2 seconds of one another.
            2. The signal-to-noise ratio (S/N) of each of the two exact m/z must be greater than or equal to 2.5:1 for a sample extract, and greater than or equal to 10:1 for a calibration standard.
            3. The ion abundance ratios must have a ratio within the limits established for the homologous series.
            4. The relative retention times of the peak for a toxic PCB must be within 5% of the relative retention times listed in Method 1668. The retention times of peaks representing PCBs other than the toxic PCBs must be within the retention time windows established
    7. Quantitative Determination
        1. For peaks that meet the criteria listed above, quantitate the PCB peaks from the mean RRF relative to the appropriate Extraction Standard established in BCS_3 or the initial calibration, as appropriate.
        2. Any peaks representing the other congeners are quantitated using the response factors from specified labeled PCBs isomers at the same level of chlorination (Table 3)
        3. Report results in picogram per gram, picogram per liter or picogram per sample.

15. DATA ANALYSIS AND CALCULATIONS

1. The concentrations for the PCBs compounds are calculated by using the formula:

$$C_X = \frac{A_X \times Q_{is}}{A_{is} \times W \times RRF}$$

Where

C_X = Concentration of unlabeled PCB congeners (or group of coeluting isomers within an homologous series) in pg/g.

A_X = Sum of the integrated ion abundances of the quantitation ions (See Table 6 of EPA Method 8290) for unlabeled PCBs.

A_{is} = Sum of the integrated ion abundances of the quantitation ion (See Table 6 of EPA Method 8290) for the labeled Extraction Standards.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

W = Weight of the sample (solid or liquid – Volume if liquid).

RRF = Calculated relative response factor for the analyte.

2. The detection limits for each absent 2,3,7,8-substituted PCDD/PCDF can be calculated using the following formula:

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$$DL = \frac{2.5 \times H_N \times Q_{is}}{H_{IS} \times W \times RRF}$$

DL = Estimated detection limit for homologous 2,3,7,8-substituted PCDD/PCDFs.

H_N = Noise height (peak to peak).

H_{IS} = Peak height of the Extraction Standard.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

W = Weight of the sample (solid or liquid).

RRF = Calculated relative response factor for the analyte.

16. METHOD PERFORMANCE

1. The method performance is thoroughly documented in our Statement of Performance, which includes the results of performance testing studies, audit samples, and international interlaboratory calibration studies.

17. POLLUTION PREVENTION

1. See Pollution Prevention Basics

18. DATA ASSESSMENT AND ACCEPTANCE CRITERIA

1. This method is performance-based. Thus, the acceptance criteria are ideally determined by the project needs through a process of negotiation with the client and any other ultimate end-user of the data. These criteria should ensure that the performance of the method is adequate for the purposes for which it is intended. The criteria will likely not resemble those used in the past. In the absence of such criteria, those outlined elsewhere within this SOP and within the published methods may be used.

2. A failure to meet all criteria does not necessarily result in a particular course of action (see next section for details). Data assessment includes a thinking process that assesses the impact of a particular analytical problem and develops the most appropriate response, in the context of the data users needs (when known). Data that do not meet all criteria for all target analytes may still be reported with relevant qualifiers and notes in the case narrative, if appropriate.

19. CORRECTIVE ACTIONS

1. Corrective actions are taken whenever needed, regardless of acceptance criteria. It is not always the case that data meeting all acceptance criteria should be accepted nor that data not meeting all criteria should be rejected.

2. When the BCS_3 fails, it is important to discern the following:

    1. The fundamental objective of the BCS_3 is to "validate" the standard solutions and spiking technique and the RRFs used to quantitatively characterize the analytes in the samples **at the time** the standards are used to prepare and analyze the samples. They are four types of standards involved in the preparation of the BCS_3 that provide various probes into assessing this "validation" procedure. They are the NS (symbolized as A_x in expressions or tables), ES, SS or CS, and JS. The question becomes how can one "extract" the information needed to complete the validation, or how does one "filter" out the irrelevant information to help with the distinction between a critical error and a minor one. A critical error means erroneous data resulting from a seriously flawed spiking technique (e.g., wrong amount of ES added under the OPR/LCS/ICAL system, or the NS under the BCS_3 system) while other minor errors can provide useful information or feedback on the measurement step (e.g., instrumentation variation). The interpretation of the information obtained from the analysis of the BCS_3 is best handled when done contextually. This analytical protocol does not claim that it offers a comprehensive analysis but merely puts forward guidelines to help the analyst in assessing the quality and reliability of the data.

    2. A failure on the "PD" requirements may be indicative of an instrumentation difficulty or spiking error. The latter can be of Level PD-1 (i.e., at the standard solution level) or Level PD-2 (i.e., at the spiking operation level). A third Level PD-3 is associated with instrumentation. An error at the NS standard solution level (Level PD-1) constitutes, under the BCS_3 system, the most serious failure and requires that a new set of standard solutions be prepared and independently validated before repeating the sample extraction and analysis, if called for by the decision flow chart ("*Thinking Method*"). Note that the decision flow charts make a distinction between short- and long-term actions. When appropriate, a new initial calibration may be required before analyzing the BCS_3 and the samples. However, if the error is a Level PD-2 error, a re-extraction and analysis is the most suitable action after correcting the flawed spiking technique. As customarily done, a new BCS_3 is prepared with a Level PD-2 error. Here again, the decision flow charts should be used since the text herein is only for illustration purposes. Distinction between Levels PD-1 and PD-2 can be accomplished contextually by examination of the initial independent validation study and control charts (showing for instance a trend suggesting a degradation of the ES solution), behavior over time charts, and/or using the matrices shown in Table Inserts 3 or 4. The Level PD-3 error is associated with instrumentation when an out-of-calibration situation is present or a temporary or localized instrumentation variation is operative. Depending on the severity of the Level PD-3 error, a new calibration (either ICAL or rerunning the BCS_3 and all the affected samples) following a new "tuning" of the instrumentation may be required (see Decision Flow Charts for "*Thinking Method*").

    3. A failure on the "RPD" requirements may be indicative of instrumentation instability or inability to sustain the instrumentation's performance over a 12-H period. Again, two levels are possible. Level RPD-1 is strictly associated with instrumentation difficulties that are unrelated to the samples under analysis. A re-analysis (i.e., re-injection) of the BCS_3 **and** of the samples can be considered as a corrective action after correction of the source of the instrumentation's shortfall (see Decision Flow Charts for "*Thinking Method*"). If

however, the re-analysis of the BCS_3 fails again, and there are indications that the spiking procedure is questionable (Level PD-1 or PD-2), the associated extraction batch may need to undergo re-extraction and analysis with the preparation of a new associated BCS3 as discussed above for the BCS_3 PD deviations. A Level RPD-2 BCS_3 failure may be found with the analysis of samples presenting special challenges (i.e., highly complex matrices that do not cleanup well under the various options offered by this protocol). Depending on the severity of the deviation, additional cleanup or other appropriate actions may be required before re-analysis of the samples and associated BCS_3. If such action proves to be ineffective, the data should be qualified accordingly.

4. A " **PD**" failure for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF results in the inability to reliably quantify 2,3,7,8-TCDD/F until proper corrective action is implemented (e.g., following GC column maintenance). When the corrective action involves a different GC column liquid phase, the **correct** BCS_3 is used to demonstrate adequate performance. Note that the laboratory is encouraged to adopt a similar stance for 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF (or any other 2,3,7,8-subtituted congeners, which significantly contribute to the TEQ and have other congeners closely eluting to them).

5. The BCS_3 "PD Requirements" are summarized in the four table inserts below. In addition to the traditional RRFs, another set of "pseudo-RRFs" is computed from the BCS3 data to help with the validation of the ES and RRFs used to report the sample analytes. The pseudo-RRFs are used to further differentiate the various "A" to "C" types PD Requirements. Use Table Insert 3 (non air) or Table Insert 4 (air) for departing-from-the-norm groups of analytes (e.g., all 17 A x or the five SS show a deviation similar in "sign" and "amplitude"). It is also recommended to examine the data contextually (e.g., using QC charts)

Table Insert 1:

Batch CS_3 PD Requirements

Based on Traditional RRFs

("A" to "C"Types)

Type	Analytes	Requirement	Failure Possible Cause[a,b]	Failure Level	Suggested Corrective Action
A	A_X vs **ES**	+ 20%	1. Calibration out 2. Spiking error	1. PD-3 2. PD-1/PD-2	3. New Calibration 4. New Standards/New Extraction
B	**ES** vs **JS**	+ 30% non air + 30% for air[c]	1. Calibration out 2. Spiking error	5. PD-3 6. PD-1/PD-2	7. New Calibration 8. New Standards/New Extraction
C_1	**CS** vs **JS**	+ 30%	1. Calibration out 2. Spiking error	9. PD-3 10. PD-1/PD-2	11. New Calibration 12. Affects other Types
C_2	**SS** vs **ES** (air)	+ 20%	1. Calibration out 2. Spiking error	13. PD-3 14. PD-1/PD-2	15. New Calibration 16. New Standards/New Extraction/New Sampling[d]

a. Calibration out = usually when one (localized) or several/all analytes are affected; instrumental source.
b. Spiking error = when all analytes are affected with the same "sign" and "amplitude"; must be considered contextually; i.e., using historical data or other information on the set of standards such as the "pseudo-RRFs". Situations when selected analytes degrade are rare but should not be excluded from consideration.
c. By design for air matrices, the amounts of ES and JS added during the preparation of the Batch CS 3 are different. Thus, an additional error is introduced, which can deceive the analyst's interpretation. In this case, the QC emphasis is shifted towards the "C2" type PD requirement.
d. Because of the nature of an "air" sample, there is no additional sample volume available to repeat the extraction. The laboratory is required to qualify the data by estimating and documenting accordingly the "error" associated with the reported measurements. If such documentation is not possible, and/or the information points toward a seriously flawed ES addition (as opposed to a spiking error associated with the SS), the data can be rejected and re-sampling efforts may be necessary. See the "Air Spiking Related Error Matrix" tables for an alternative approach whereby the A_X vs SS RRFs are used to determine the analyte's concentrations (Table Insert 4).

Table Insert 2 :

Batch CS_3 PD Requirements

Based on Pseudo-RRFs

("D" to "G"Types)

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Type	Analytes[a]	Requirement
D	A_x vs CS/SS	+/- 25%
E_1	A_x vs JS (non air)	+/- 35%
E_2	A_x vs JS (air)	+/- 35%
F_1	ES vs CS (non air)	+/- 20%
G_2	SS vs JS (air)	+/- 50%

a. Pseudo-RRFs are limited to analytes, for which an analogous/homologous standard is available:

Table Insert 3:

"Non-Air" Spiking Related PD Errors

(departing-from-the-norm group of analytes)

"PD Requirements Decision Matrix" – Normal Configuration
(use BCS_3 RRFs)

	Ax	ES	CS	JS
Ax	-	Y	Y	Y
ES	-	-	Y	Y
CS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective A_x Spiking = Fatal
(If A_x spiking is shown to be in error, and if no additional or replacement sample is available, use ICAL RRFs if CS_3 is acceptable)

	Ax	ES	CS	JS
Ax	-	N	N	N
ES	-	-	Y	Y
CS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective JS Spiking
(use BCS_3 RRFs)
percent recovery measurements for CS & ES affected, not the analytes

	Ax	ES	CS	JS
Ax	-	Y	Y	N
ES	-	-	Y	N
CS	-	-	-	N

"PD Requirements Decision Matrix" – Defective CS Spiking
(use BCS_3 RRFs)
percent recovery measurements for CS affected, not the analytes

	Ax	ES	CS	JS
Ax	-	Y	N	Y
ES	-	-	N	Y
CS	-	-	-	N

"PD Requirements Decision Matrix" – Defective ES Spiking
(use BSC_3 RRFs; see Levels PD-1 or PD-2)

	Ax	ES	CS	JS
Ax	-	N	Y	Y
ES	-	-	N	N
CS	-	-	-	Y

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Table Insert 4:

"Air" Spiking Related PD Errors

(departing-from-the-norm group of analytes)

"PD Requirements Decision Matrix" – Normal Configuration
(use BCS_3 RRFs)

	Ax	ES	SS	JS
Ax	-	Y	Y	Y
ES	-	-	Y	Y
SS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective A_x Spiking = **Fatal**
(If Ax spiking is shown to be in error, and if no additional or replacement)

	Ax	ES	SS	JS
Ax	-	N	N	N
ES	-	-	Y	Y
SS	-	-	-	Y

"PD Requirements Decision Matrix" – Defective JS Spiking
(use BCS_3 RRFs)
percent recovery measurements for ES affected, not the analytes or the SS

	Ax	ES	SS	JS
Ax	-	Y	Y	N
ES	-	-	Y	N
SS	-	-	-	N

"PD Requirements Decision Matrix" – Defective SS Spiking
(use BCS_3 RRFs)
percent recovery measurements for SS affected, not the analytes

	Ax	ES	SS	JS
Ax	-	Y	N	Y
ES	-	-	N	Y
SS	-	-	-	N

"PD Requirements Decision Matrix" – Defective ES Spiking
(use BCS_3 RRFs; see Levels PD-1 or PD-2; for air samples only, consider using the A_x vs SS RRFs)

	Ax	ES	SS	JS
Ax	-	N	Y	Y
ES	-	-	N	N
SS	-	-	-	Y

Decision Flow Charts for "*Thinking Method*"

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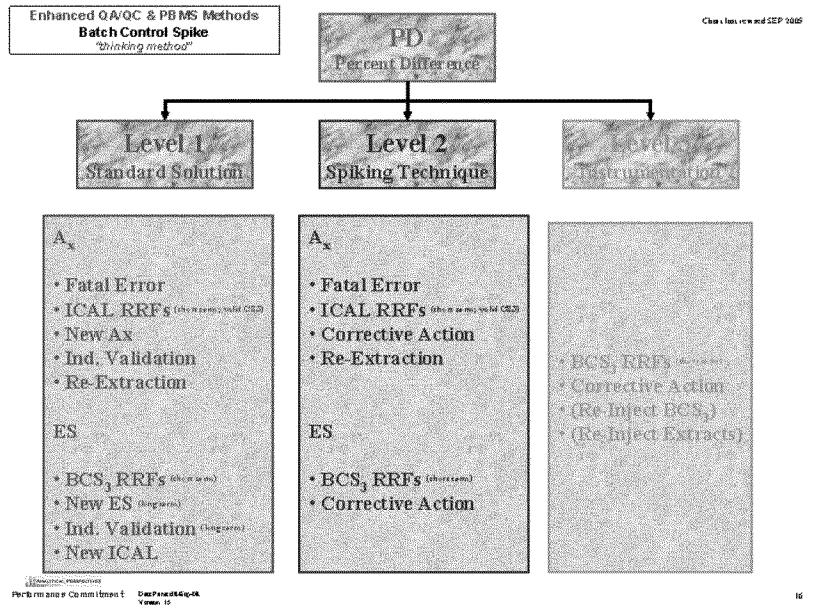

Enhanced QA/QC & PBMS Methods
Batch Control Spike
"thinking method"
PD
Percent Difference
Level 1
Standard Solution
Level 2
Spiking Technique
Level 3
Instrumentation
A_x
• Fatal Error
• ICAL RRFs
• New Ax
• Ind. Validation
• Re-Extraction
ES
• BCS_3 RRFs
• New ES
• Ind. Validation
• New ICAL
A_x
• Fatal Error
• ICAL RRFs
• Corrective Action
• Re-Extraction
ES
• BCS_3 RRFs
• Corrective Action
• BCS_3 RRFs
• Corrective Action
• (Re-Inject BCS_3)
• (Re-Inject Extracts)
Performance Commitment
16

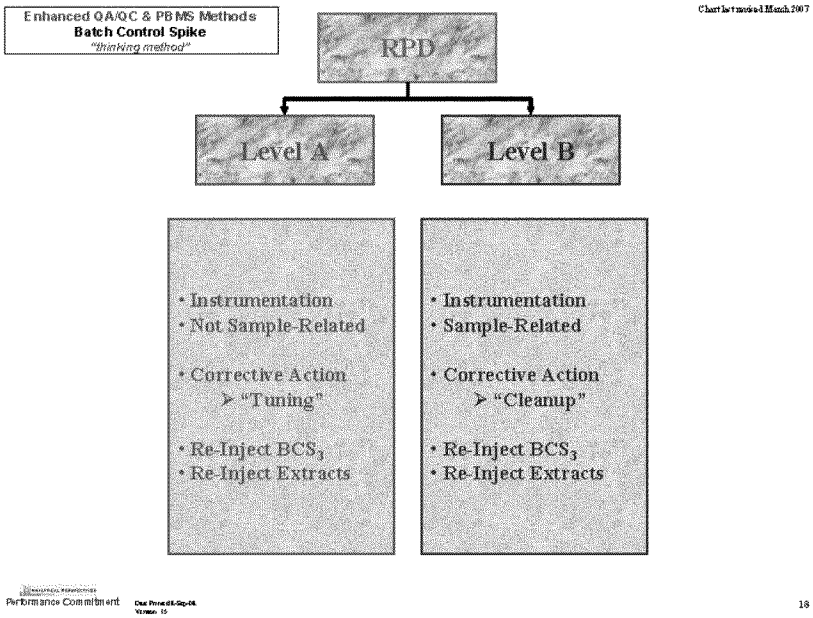
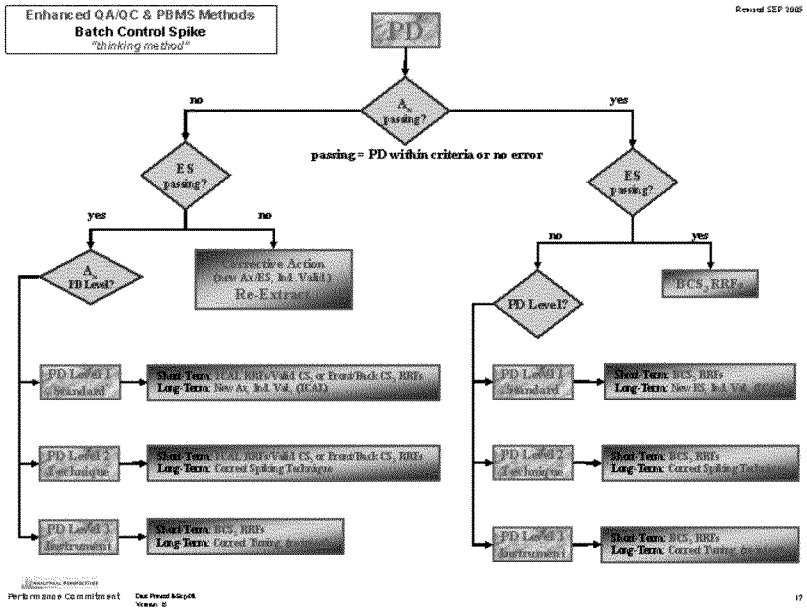


Chart last revised March 2007
Enhanced QA/QC & PBMS Methods
Batch Control Spike
"thinking method"
RPD
Level A
Level B
• Instrumentation
• Not Sample-Related
• Corrective Action
➢ "Tuning"
• Re-Inject BCS_3
• Re-Inject Extracts
• Instrumentation
• Sample-Related
• Corrective Action
➢ "Cleanup"
• Re-Inject BCS_3
• Re-Inject Extracts
Performance Commitment
18

CBI



20. CONTINGENCIES FOR HANDLING OUT -OF-CONTROL OR UNACCEPTABLE DATA

1. Should data be found unacceptable after a thorough assessment, the appropriate corrective action will be taken. In the case that the appropriate corrective action requires reextraction of exhausted samples, the client will be contacted for consultation with regard to the next steps to be taken.

21. WASTE MANAGEMENT

1. The storage and disposal of wastes generated by this method is covered in our Health and Safety SOPs.

22. REFERENCES

Method 1668B. Measurement of Toxic PCB Congeners By Isotope Dilution HRGC/HRMS, Prepared by Analytical Methods Staff, Engineering and Analysis Division, Office of Science and Technology, Office of Water, U. S. Environmental Protection Agency, Washington, DC, November 2008.

23. TABLES AND NOTES

Table 1. Concentration of PCBs in Calibration and Calibration Verification Solutions

1668A ICAL units: pg/µL							
Individual Standard	IUPAC	CS0	CS-1	CS-2	CS-3 VER	CS-4	CS-5
2-MoCB	1	0.5	L0	5.0	50	400	2000
4-MoCB	3	0.5	L0	5.0	50	400	2000
2,2'-DiCB	4	0.5	L0	5.0	50	400	2000
4,4'-DiCB	15	0.5	L0	5.0	50	400	2000
2,2',6-TrCB	19	0.5	L0	5.0	50	400	2000
3,4,4'-TrCB	37	0.5	L0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.5	L0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.5	L0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.5	L0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.5	L0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.5	L0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.5	L0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.5	L0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.5	L0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.5	L0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.5	L0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.5	L0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.5	L0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.5	L0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.5	L0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.5	L0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.5	L0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.5	L0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.5	L0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.5	L0	5.0	50	400	2000
2,2',3,3',4,5,5',6,6'-NoCB	208	0.5	L0	5.0	50	400	2000
DeCB	209	0.5	L0	5.0	50	400	2000

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1668A ICAL units: pg / µL Individual Standard	IUPAC	CS0	CS-1	CS-2	CS-3 VER	CS-4	CS-5
Extraction Standards							
13C12-3-MoCB	1 L	100	100	100	100	100	100
13C12-4-MoCB	3 L	100	100	100	100	100	100
13C12-2,2'-DiCB	4 L	100	100	100	100	100	100
13C12-4,4'-DiCB	15 L	100	100	100	100	100	100
13C12-2,2',5-TrCB	19 L	100	100	100	100	100	100
13C12-3,4,4'-TrCB	37 L	100	100	100	100	100	100
13C12-2,2',5,5'-TeCB	54 L	100	100	100	100	100	100
13C12-3,3',4,4'-TeCB	77 L	100	100	100	100	100	100
13C12-3,4,4',5-TeCB	81 L	100	100	100	100	100	100
13C12-2,2',4,4',5-PeCB	104 L	100	100	100	100	100	100
13C12-2,3,3',4,4'-PeCB	105 L	100	100	100	100	100	100
13C12-2,3,4,4',5-PeCB	114 L	100	100	100	100	100	100
13C12-2,3',4,4',5-PeCB	118 L	100	100	100	100	100	100
13C12-2',3,4,4',5-PeCB	123 L	100	100	100	100	100	100
13C12-3,3',4,4',5-PeCB	126 L	100	100	100	100	100	100
13C12-2,2',4,4',5,5'-HxCB	153 L	100	100	100	100	100	100
13C12-2,3,3',4,4',5-HxCB	156 L	100	100	100	100	100	100
13C12-2,3,3',4,4',5'-HxCB	157 L	100	100	100	100	100	100
13C12-2,3',4,4',5,5'-HxCB	167 L	100	100	100	100	100	100
13C12-3,3',4,4',5,5'-HxCB	169 L	100	100	100	100	100	100
13C12-2,2',3,4',5,5',6-HpCB	188 L	100	100	100	100	100	100
13C12-2,3,3',4,4',5,5'-HpCB	189 L	100	100	100	100	100	100
13C12-2,2',3,3',5,5',6,6'-OcCB	202 L	100	100	100	100	100	100
13C12-2,3,3',4,4',5,5',6-OcCB	205 L	100	100	100	100	100	100
13C12-2,2',3,3',4,4',5,5',6-NoCB	206 L	100	100	100	100	100	100
13C12-2,2',3,3',4',5,5',6,6'-NoCB	208 L	100	100	100	100	100	100
13C12-DeCB	209 L	100	100	100	100	100	100
Cleanup or Sampling Standards							
13C12-2,4,4'-TrCB	28 L	100	100	100	100	100	100
13C12-2,3,3',5,5'-PeCB	111 L	100	100	100	100	100	100
13C12-2,2',3,3',5,5',6-HpCB	178 L	100	100	100	100	100	100
Injection Standards							
13C12-2,6-DiCB	9 L	100	100	100	100	100	100
13C12-2,2',5,5'-TeCB	52 L	100	100	100	100	100	100
13C12-2,2',4,5,5'-PeCB	101 L	100	100	100	100	100	100
13C12-2,2',3,4,4',5'-HxCB	138 L	100	100	100	100	100	100
13C12-2,2',3,3',4,4',5,5'-OcCB	194 L	100	100	100	100	100	100

Table 2. Theoretical Ion Abundance Ratios and QC Limits (Regular Initial Calibration)

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits[1]	
			Lower	Upper
1	M/M+2	3.13	2.66	3.60
2	M/M+2	1.57	1.33	1.81
3	M/M+2	1.04	0.88	1.20
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.56	1.32	1.78
6	M/M+2	0.51	0.43	0.59
6	M+2/M+4	1.25	1.05	1.43
7	M/M+2	0.45	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02
9	M/M+2	1.34	1.14	1.54
9	M/M-2	0.78	0.66	0.90
10	M/M+2	1.17	0.99	1.35

Table 3. Quantitation References for Analytes

CB

AP Quantitation References

ES PCB-1	ES PCB-4	ES PCB-19	ES PCB-54	ES PCB-104	ES PCB-155	ES PCB-188	ES PCB-202	ES PCB-206
PCB-1	PCB-4	PCB-19	PCB-54	PCB-104	PCB-155	PCB-188	PCB-202	PCB-206
	PCB-10	PCB-30/18		PCB-96	PCB-152	PCB-179	PCB-201	
ES PCB-3		PCB-17	ES PCB-77		PCB-150 PC	B-184	PCB-204	ES PCB-208
PCB-2	ES PCB-15	PCB-27	PCB-77	ES PCB-105	PCB-136 PC	B-176 PC	B-197	PCB-208
PCB-3	PCB-9	PCB-24		PCB-105	PCB-145	PCB-186	PCB-200	PCB-207
	PCB-7	PCB-16	ES PCB-81	PCB-127		PCB-178	PCB-198/199	
	PCB-6 PC	B-32	PCB-52		ES PCB-153		PCB-196	
	PCB-5		PCB-73	ES PCB-114	PCB-148	ES PCB-180	PCB-203	
	PCB-8	ES PCB-37	PCB-43 PC	B-122	PCB-151/135	PCB-175		
	PCB-14	PCB-34	PCB-69/49	PCB-114	PCB-154	PCB-187	ES PCB-205	
	PCB-11	PCB-23	PCB-48		PCB-144	PCB-182	PCB-195	
	PCB-13/12	PCB-26/29	PCB-44/47/65	ES PCB-118	PCB-147/149	PCB-183	PCB-194	
	PCB-15	PCB-25	PCB-59/62/75	PCB-118	PCB-134	PCB-185	PCB-205	
		PCB-31	PCB-42		PCB-143	PCB-174		
		PCB-28/20	PCB-41	ES PCB-123	PCB-139/140 PCB-	177		
		PCB-21/33 PC	B-71/40 PC	B-103	PCB-131	PCB-181		
		PCB-22	PCB-64 PC	B-94 PC	B-142	PCB-171/173		
		PCB-36	PCB-72	PCB-95	PCB-132	PCB-172		
		PCB-39	PCB-68	PCB-100/93	PCB-133	PCB-192		
		PCB-38	PCB-57	PCB-102	PCB-165	PCB-180/193		
		PCB-35	PCB-58	PCB-98	PCB-146	PCB-191		
		PCB-37	PCB-67	PCB-88	PCB-161			
			PCB-63	PCB-91	PCB-153/168	ES PCB-170		
			PCB-61/70/74/76	PCB-84	PCB-141	PCB-170		
			PCB-66	PCB-89	PCB-130	PCB-190		
			PCB-55	PCB-121	PCB-137			
			PCB-56 PC	B-92	PCB-164			
			PCB-60	PCB-113/90/101	PCB-163/138/129			
			PCB-80	PCB-83	PCB-160	ES PCB-189		
			PCB-79	PCB-99	PCB-158	PCB-189		
			PCB-78	PCB-112				
			PCB-50/53* P	CB-108/119/86/97/125/87				
			PCB-45*	PCB-117	ES PCB-156/157			
			PCB-51* PC	B-116/85	PCB-156/157			
			PCB-46*	PCB-110				
			PCB-81	PCB-115	ES PCB-167			
				PCB-82	PCB-128/166			
				PCB-111	PCB-159			
				PCB-120 PC	B-162			
				PCB-107/124	PCB-167			
				PCB-109				
				PCB-123	ES PCB-169			
				PCB-106 PC	B-169			
				ES PCB-126				
				PCB-126				

Note: Quantitation Reference for those congeners without a Labeled Standard is based on the nearest ES @ the same level of chlorination within the same function.
Quantitation of those congeners within a function where there is no ES is based on the nearest ES in the other functions of that homologue .
** Based on analytical observations PCB's 50/53, 45,51& 46 were moved to ES 81 when the additional ES's were added.*

Table 4. Quantitation References for Extraction Standards

ES/JS Quantitation References					CS/JS Quantitation References		
ES 188 & 202 were originally quantitated against JS 194 - based on analytical observations JS 138 was determined a better choice							
JS PCB-9	**JS PCB-52**	**JS PCB-101**	**JS PCB-138**	**JS PCB-194**	**CS PCB-28**	**CS PCB-111**	**CS PCB-178**
ES PCB-1	ES PCB-37	ES PCB-104	ES PCB-155		JS PCB-52	JS PCB-101	JS PCB-138
ES PCB-3	ES PCB-54	ES PCB-105	ES PCB-156/157	ES PCB-189			
ES PCB-4	ES PCB-77	ES PCB-114	ES PCB-167				
ES PCB-15	ES PCB-81	ES PCB-118	ES PCB-169	ES PCB-205			
ES PCB-19		ES PCB-123	ES PCB-188*	ES PCB-206	**SS PCB-28**	**SS PCB-111**	**SS PCB-178**
		ES PCB-126	ES PCB-202*	ES PCB-208	JS PCB-37	JS PCB-123	JS PCB-188
				ES PCB-209			

List of Abbreviations &Acronyms

CBI

1. AS = alternate standard
2. A_x = target analyte
3. BCS_3 = batch control spike
4. CAA = Clean Air Act
5. COC = chain of custody
6. CPSM = column performance standard mixture
7. CS_3 = calibration solution corresponding to the middle point of the initial calibration curve
8. CS = cleanup standard
9. CWA = Clean Water Act
10. *dfa* Technology = dioxin-furan array (fingerprinting reminiscent of DNA plates)
11. DOC = documentation of capability
12. DUP = duplicate
13. EDL = estimated detection limit (sample- and analyte-specific)
14. ES = extraction standard (isotopically labeled standard added before the extraction)
15. GC = gas chromatography
16. ICAL = initial calibration
17. ID-HRMS = comprehensive and stable isotope-dilution high-resolution mass spectrometry
18. Ind. Val. = independent validation
19. JS = injection standard
20. LOD = limit of detection
21. LOQ = limit of quantitation
22. MB = lab method blank
23. MDL = method detection limit (not sample-specific)
24. M/ΔM = mass spectrometer resolving power
25. MIR = Methods Innovation Rule
26. ML = minimum level (equivalent to lowest point on the calibration curve)
27. MS/MSD = matrix spike/matrix spike duplicate
28. ND = not detected
29. NELAC = National Environmental Laboratory Accreditation Conference
30. OPR = on-going precision & recovery (equivalent to LCS or Lab Control Spike)
31. PAH = polynuclear aromatic hydrocarbon
32. PBMS = performance-based measurement system
33. PCB = polychlorinated biphenyl
34. PCDD/F = polychlorinated dibenzo-*p*-dioxin and dibenzofuran
35. PD = percent difference
36. PE = performance evaluation sample
37. QI = quantitative interference
38. QuanTIC = selected SVOAs by full-scan GC/MS (ID-HRMS)
39. RCRA = Resources Recovery Act
40. RL = reporting limit (usually represents the lowest point on the calibration curve or ML)
41. RPD = relative percent difference
42. RRF = relative response factor
43. RSD = relative standard deviation
44. RTW = retention time defining window solution
45. SDWA = Safe Drinking Water Act
46. SICP = selected ion current profile
47. S/N = signal-to-noise ratio
48. SRM = standard reference material
49. SS = sampling standard
50. TEQ = toxic equivalency quotient
51. TSCA = Toxic Substances Control Act
52. U-SVOA = ultra-semi volatile analyte (selected SVOAs by SIR by ID-HRMS)
53. VER = continuing calibration verification (equivalent to ConCal)
54. WHO-2 / WHO-2S = ID-HRMS assay for the 29 World Health Organization target analytes (S = serum)

SOP No. AP-CM-14	Revision: 1	Effective: 22 MAY 12	Supercedes: N/A
PCB HIGH VOLUME SAMPLING ADDENDUM **USEPA METHODs 1668A/B/C**			
Author: Julie Martin			
Management – Bryan Vining, Ph.D. 22 MAY 12			
QA Officer - Bryan Vining, Ph.D. 22 MAY 12			

Unless otherwise listed here, these samples shall be processed and analyzed according to the procedures and methods stated in the appropriate Analytical Perspectives SOPs. This procedure augments SOP AP-CM-7, Revision 9-1.

New spiking solutions as well as new terms were created for this procedure.

This procedure creates multi-component samples analogous to air samples; the extraction of these samples follows the same air extraction procedures used when no split or archive is required (See section 14.1.6 of SOP AP-CM-7, Revision 9-1.

The following text and tables augment section 19 of SOP AP-CM-7, Revision 9-1.

RECOVERY LIMITS:

RECOVERY LIMITS FOR THE PCB DS_{FS} AND SS SPIKES

Spiking Solution	% Recovery
DS_{FS} spike (MeOH)	25% - 150%
SS spike	50% - 150%

The following text and tables augment section 23 of SOP AP-CM-7, Revision 9-1.

DYNAMIC STANDARD (DS_{FS}): A SPIKE USED IN THE FIELD TO DETERMINE HOW WELL THE HVS PROCEDURE RECOVERS SPECIFIC ANALYTES DURING THE SAMPLING PROCESS. METHANOL IS USED AS THE CARRIER SOLVENT.

PCB DS_{FS} SPIKE SOLUTION CONSTITUENTS

Compound	Dynamic Spike Standards Amount Spiked ng
$^{13}C_{12}$ – 2,4'-DiCB (PCB-8)	2
$^{13}C_{12}$ - 2,4,5,-TriCB (PCB-31)	2
$^{13}C_{12}$ - 2,3,4,4'-TeCB (PCB-60)	2
$^{13}C_{12}$ -2,2',3,4,4'-PeCB (PCB-85)	2
$^{13}C_{12}$ -2,2',3,3',4,4'-HxCB (PCB-128)	2

STATIC STANDARD (SS): IDENTICAL IN COMPOSITION TO THE SAMPLING STANDARD USED FOR OTHER PROCEDURES. THE SS IS SPIKED INTO THE SORBENT PRIOR TO SAMPLING.

PCB SS SOLUTION CONSTITUENTS

Compound	Static Spike Standards Amount Spiked (ng)
$^{13}C_{12}$ -2,4,4'-TrCB (PCB-28)	2
$^{13}C_{12}$ - 2,3,3',5,5'-PeCB (PCB-111)	2
$^{13}C_{12}$ - 2,2',3,3',5,5',6-HpCB (PCB-178)	2

ALTERNATE CLEANUP STANDARD (AS_{PCB}): USED IN LIEU OF THE USUAL CS COMPOUNDS, SINCE THE CS COMPOUNDS ARE USED AS SS IN THIS APPLICATION.

PCB AS_{PCB} SPIKE SOLUTION CONSTITUENTS

Compound	Alternate Cleanup Standards Amount Spiked ng
$^{13}C_{12}$ – 2,4',6-TriCB (PCB-32)	2
$^{13}C_{12}$ - 2,2',3',4,5-PeCB (PCB-97)	2
$^{13}C_{12}$ -2,2',3,4,5,5'-HxCB (PCB-141)	2

STANDARD OPERATING PROCEDURE

TOTAL ORGANIC CARBON IN WATER

GEN-TOC
Revision 11
February 29, 2010

Approved By:

Supervisor	2/5/10 Date
QA Manager	2/8/10 Date
Laboratory Manager	2/8/10 Date

COLUMBIA ANALYTICAL SERVICES, INC.
1317 South 13th Avenue
Kelso, Washington 98626

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL

NUMBER: _____

Initials: _____ Date: _____

Total Organic Carbon in Water

1 SCOPE AND APPLICATION

1.1 This procedure is applicable to the determination of Total Organic Carbon (TOC) in drinking, surface and saline waters, domestic and industrial wastewater using methods EPA 9060A, and Standard Methods 5310C, 20th Edition. The procedure may also be extended to certain domestic or industrial wastes.

1.2 This procedure may be modified for quantification of Dissolved Organic Carbon (DOC) where TOC is determined from a filtered sample. Refer to section 6 for guidance on proper handling and preservation of DOC samples.

1.3 Normal operating parameters (i.e. 1 ml sample loop) yield a Method Reporting Limit (MRL) of 0.5 ppm C. A 5 ml sample loop may be used to lower the MRL to 0.1 ppm C. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL) and Practical Quantitation Limit (PQL). Therefore, MRL=EQL=PQL. The Method Detection Limit currently determined for a water matrix is 0.1 ppm.

1.4 In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP. QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD)* may supersede the requirements defined in this SOP.

2 METHOD SUMMARY

2.1 Total Organic Carbon (TOC) is determined by measuring carbon dioxide released by chemical oxidation of the non-purgeable organic carbon in the sample. After the sample has been acidified and purged of inorganic carbon, sodium persulfate, a strong oxidizer, is added. This oxidant quickly reacts with non-purgeable organic carbon in the sample at 100°C to form carbon dioxide. When the reaction is complete, the carbon dioxide is purged from the solution, concentrated by trapping then thermally desorbed (200°C) and carried into a non-dispersive infrared detector that has been calibrated to directly display the mass of carbon dioxide detected. The resulting carbon mass in the form of carbon dioxide is the equivalent to the mass of organic carbon originally in the sample.

2.2 Total Inorganic Carbon is determined by carbon dioxide released by acidification of a sample. The pH of the sample is lowered; carbonate and bicarbonate ions are converted to dissolved carbon dioxide. This carbon dioxide is purged from the solution, concentrated by trapping, and detected as described for TOC.

3 DEFINITIONS

3.1 Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc...) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2 Independent Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration. The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards.

3.3 Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Samples are split into duplicates, spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at 25 mg/L or at levels specified by a project analysis plan.

3.4 Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.5 Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.6 Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of

contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

4 INTERFERENCES

4.1 Carbonate and bicarbonate carbon are interferences under the terms of this test and must be removed or accounted for in the final calculations.

4.2 This procedure is applicable only to homogenous samples that can be injected reproducibly by microliter type syringe or pipette. The opening of the syringe or pipette limits the size of particles which may be included in the samples (both the Model 1700 and Model 1010 analyzers can analyze samples with suspended solids up to 500 microns diameter).

4.3 Positive bias may be caused by contaminants in the gas, dilution water, reagents, glassware, or other sample processing hardware. The use of high purity reagents and gases help minimize interference problems. Materials may be demonstrated to be free from interference by running reagent blanks.

4.4 Interference by non-CO2 gases: The infrared detector is sensitized to carbon dioxide and accomplishes virtually complete rejection of response from other gases which absorb energy in the infrared region. Trapping and desorption of carbon dioxide on the molecular sieve trap isolates the component of interest and allows the complete absence of interference in the system from gases other than carbon dioxide.

5 SAFETY

5.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2 Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3 Always wear chemical eye, skin, and clothes protection when handling samples or working with reagents.

5.4 Sodium Persulfate is a strong oxidizer and should be handled with extreme care.

5.5 Phosphoric Acid is a corrosive material should be handled with extreme care.

5.6 Potassium Biphthalate and Sodium Carbonate are chemical irritants and may cause eye burns.

6 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1 For most accurate analyses, sampling containers should be free of organic contaminants.

6.2 Sampling and storage of samples in glass bottles is preferable. If this is not feasible, sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.

Note: A brief study performed at the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

6.3 For samples requiring very low-level TOC analysis (below about 50 ppb C) consult appropriate literature for sample handling and storage.

6.4 Because of the possibility of oxidation or bacterial decomposition of certain components in aqueous samples, the time between sample collection and analysis should be minimized. In addition, the samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

6.5 In situations where analysis cannot be performed within two hours (2 hours) of sampling, the sample must be acidified (pH < 2) with HCL or H_2SO_4. Once preserved, samples must be analyzed within 28 days.

6.6 Samples requiring DOC analyses should be filtered through a prewashed 0.45 micron glass microfiber membrane filter prior to acid preservation. A DI water filter blank should also be included with the filtration batch to determine potential for sample contamination from filter or filtration apparatus.

7 APPARATUS AND EQUIPMENT

7.1 Model 1010 Total Organic Carbon Analyzer: Utilizes classic persulfate oxidation method. (O.I. Analytical)

7.2 Autosampling Capability, Model 1010: 88-sample capacity, (model 1051).

7.3 Apparatus for blending or homogenizing samples.

Note: Homogenization: Prior to analysis, the sample is thoroughly mixed by shaking the sample in the bottle rather than blending the sample. The concern is for possible contamination from the blender. It is not considered that this will misrepresent the true best average of the sample. The Model 1051 autosampler has magnetic stirring capability that homogenizes the sample prior to injection.

8 STANDARDS, REAGENTS, AND MATERIALS

8.1 Reagent (laboratory deionized water

8.2 Potassium Biphthalate (KHP) stock solutions

8.2.1 1000 ppm C stock solution is prepared by adding 2.128 g of KHP (previously dried to a constant weight at 105°C) into a 1000 ml volumetric flask. Dilute to volume with reagent water. Solution contains 1.0 ug C per ul.

8.2.2 5000 ppm C stock solution is prepared by adding 10.64 g of KHP (previously dried to a constant weight at 105°C) into a 1000 ml volumetric flask. Dilute to volume with reagent water. Solution contains 5.0 ug C per ul.

Note: Stock solution has a shelf life of six months after preparation. Sodium oxalate and acetic acid are not recommended as stock solutions.

8.2.3 Linear range verification solutions at a minimum 5 concentrations, typically 0.05-50 ppm are prepared by diluting appropriate amounts of the 1000 mg/L stock standard to 100 mls with reagent grade water. These standards should be prepared fresh each time a multi-point calibration is performed.

8.3 Sodium Carbonate Stock solution (1000 ppm C) - Prepare stock solution by adding 8.826 g of Na_2CO_3 (previously dried to a constant mass at 105°C) to a 1000 ml volumetric flask. Dilute to volume with reagent water. Solution contains 1.0 ug C per ul.

8.4 Sodium Persulfate (250 g/L) - Prepare solution of sodium persulfate by dissolving 250g $Na_2S_2O_8$ into preheated reagent water (1 liter volume). Reagent has a shelf life of one month.

Note: Reagent water is heated until solution just comes to a boil. Once reagent water has come to a boil, remove from heat and add sodium persulfate (250 g). Stir until persulfate goes into solution, then immediately cool by running water over the outside of beaker. This procedure purifies the $Na_2S_2O_8$ solution by reducing TOC content of reagent water. Once cool, place the Model 700 purge lines in solution to remove any CO2 from oxidation of organics. Alternatively, dissolve sodium persulfate (250g) in 1L reagent water and purge with nitrogen for 5-10 minutes before use.

8.5 Phosphoric Acid (5%) - Prepare 5% by volume solution of phosphoric acid by adding 59 ml of ACS reagent grade 85% H_3PO_4 to reagent water (1 liter total volume). Reagent has a shelf life of one month.

8.6 The ICV is prepared by diluting 2.0 mL of 5000 ppm KHP stock solution to 200 mL DI water in a class A volumetric flask. Resulting concentration is 20.0 ppm. For low level analysis, dilute 2.0 mL of the 1000 ppm KHP stock solution to 1L DI water in a class A volumetric flask. Resulting concentration is 2.0 ppm. The shelf life is 6 months.

8.7 Continuing Calibration Verification (CCV) - The CCV is prepared by diluting 5.0 mls of 5000 ppm KHP stock solution (see 8.2) to 1000 mls in a class A volumetric flask. Resulting concentration is 25.0 ppm. For low level analysis, dilute 5.0 mls of the 1000 ppm KHP stock solution to 1000 mls in a class A volumetric flask. The shelf life is 6 months.

8.8 Laboratory Control Sample (LCS) - The LCS is prepared from Demand APG (Analytical Products Group). The true value is determined based on the lot number of the standard. The resulting standard has a shelf life of six months unless APG has a predetermined expiration date which expires prior to six months.

8.9 Gas Service: Nitrogen

9 PREVENTIVE MAINTENANCE

9.1 For the most reliable performance of the instrument, the following schedule of routine maintenance is suggested:

Weekly:

- Replace gas cylinder
- Adjust IR "zero"
- Leak-check the carrier and purge gases
- Check tube end fitting connections

Quarterly:

Replace or clean the permeation tube
Clean the digestion vessel
Check indicating drying tube
Check sample pump

Semi-annually:

Clean NDIR cell

Annually:

NDIR linearization check

9.2 Record any maintenance procedures performed in a maintenance logbook. Initial and date all entries.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2 It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Technical Personnel Training is also the responsibility of the department supervisor/manager.

11 PROCEDURE

11.1 Turn on the nitrogen gas flow and confirm delivery pressure (50-60psi). Maintain this delivery pressure. If pressure drops to below 15 psi, the instrument will automatically shut down.

11.2 Initial Power Up

11.2.1 Turn on power to the Model 1010 analyzer, Model 1051 autosampler and computer using the main power switches.

11.2.1.1 During the Model 1010 power-up, listen for a series of beeps to determine the status of the instrument. The beep sequence is 1 beep=

system startup, 2 beeps= CMOS check passed and 3 beeps= Firmware ready. If the beeps are not heard, contact OI Analytical Service Department for assistance.

11.2.1.2 Log into the WinTOC program. The user name is "user" and the password is "toc." Select TOC1 for operation.

11.2.2 To obtain a stable baseline, a reagent blank sequence must be started.

11.2.2.1 From the 'Setup' drop down, select WinTOC output. Change file names to reflect the date of analysis.

11.2.2.2 Select the reagent blank sequence from the 'Sequence' drop down.

11.2.2.3 Ensure that the most recent calibration check is selected from the 'Calibration' drop down.

11.2.2.4 Ensure that the TOC method is selected from the Database menu.

11.2.2.5 Click the start button on the status screen to begin the reagent blank sequence.

11.2.2.6 A stable baseline is obtained when the area counts are in the range of 50 to 200, and the last three area counts are within 50 counts of each other.

11.2.2.7 Once these criteria are met, abort the reagent blank sequence by clicking 'Abort' on the status screen.

11.2.3 An analysis sequence may now be started.

11.2.3.1 Select the run sequence desired from the 'Sequence' drop down.

11.2.3.2 Enter samples and standards in the selected run sequence.

11.2.3.3 Load tray into autosampler and click start on the status screen.

11.3 Calibration

11.3.1 The infrared detector response has been linearized and is fixed. A single point calibration verification is performed. Consult page 63 of the model 1010 user manual, for the proper calibration procedure.

11.3.1.1For routine analyses (i.e. 1 ml sample loop) a 25 ppm standard is used for calibration.

11.3.1.2For low level analyses (i.e. 5 ml sample loop) a 5 ppm standard is used for calibration.

11.3.2 Although the infrared detector response has been linearized, a series of five linear range verification standards are analyzed annually to confirm that the instrument is giving accurate readings over the working range of the analysis.

11.3.2.1Analyze each of the linear range verification standards and check each result against the true value.

11.3.2.2A least squares linear regression is performed on mean area pairs (see Appendix B). From the slope of the regression line a response factor is calculated as ug C per thousand area counts. A correlation coefficient is also calculated and must be **$\geq$0.995**. The carbon mass from the reagent water is determined from the y-intercept of the regression line.

11.3.2.3If the results indicate a non-linear response over the range, corrective action is necessary. This may include maintenance and/or recalibration. Maintain documentation of the linear range verification.

11.3.3 An ICV is analyzed following the initial calibration prior to sample analysis. Recovery must be **90-100%** of the true value.

11.3.4 A CCV must be analyzed following every tenth injection and at the end of the run. The CCV is a 25.0 ppm TOC Standard made from stock KHP solution (see 8.2). Recovery must be **90-110%** of the value (**91-106% for Arizona** samples). For low level analyses (i.e. 0.1ppm MRL), the CCV is a 5.0 ppm standard. Calculate the CCV recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Measured concentration of the CCV
TV = True value of CCV

11.3.5 A CCB must be analyzed following every CCV. The CCB is D.I. water, and the result must be below the MRL.

11.4 Sample Analysis

11.4.1 Once system configurations have been established and baseline is stable, the instrument is ready for analysis.

11.4.2 Reagent blank counts must be between 50 and 500 counts. The last 3 counts must be within 50 counts of each other.

11.4.3 Load samples into Autosampler vials and arrange them according to the analytical run sequence shown below. Samples containing suspended solids must be thoroughly mixed prior to sampling.

11.4.4 Analytical Run Sequence. Click Start on the model 1010 to begin analysis. Analyze samples in analysis sequence as listed below.

11.4.5 When performing method 5310C, analyze all samples in duplicate. The measurements must be within ±10%. If not, repeat the analysis until consecutive are obtained that are reproducible to within ±10%. Since this is a analytical step required to generate the reported result, this also applies to PT samples

11.4.6 When performing method 9060A, analyze all samples in quadruplicate. Since this is a analytical step required to generate the reported result, this also applies to PT samples

Step	Sample
1	ICV
2	ICB
3	CCV-1
4	CCB-1
5	Method blanke
6	LCS
7	Sample
8	Sample-Dup
9	Sample-Spk
10	Rinse blank
11	Rinse blank
12	Sample
13	Sample
14	Sample
15	CCV-2
16	CCB-2

12 QA/QC REQUIREMENTS

12.1 Initial Precision and Recovery Validation

12.1.1 The ability of each analyst/instrument to generate acceptable accuracy and precision must be documented validated and documented before analysis of samples begins, or whenever significant changes to the procedures have been made To do this, four water samples are spiked with the LCS spike solution, then prepared and analyzed. Method criteria must be met for these results.

12.2 Method Detection Limits and Method Reporting Limits

12.2.1 A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.2.2 Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to the CAS *SOP Performing Method Detection Limit Studies and Establishing Limits of detection and Quantification (ADM-MDL).* The MDL study must be verified annually.

12.2.3 The Method Reporting Limits (MRLs) used at CAS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which CAS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3 Ongoing QC Samples each sample batch (20 or fewer samples) required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD).* General QC Samples are:

12.3.1 A laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. The LCS is prepared from a standard which is an independent

source from the calibration standards. Results must be **90-109%** of the certified value. This statistically derived acceptance limit is subject to change as limits are updated.

Note: When performing Method 9060 analysis, the second source LCS must be analyzed every 15 samples rather than every 20 samples.

Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value or amount spiked

12.3.2 A method blank (Deionized Water) must be analyzed with each batch of 20 or fewer samples. The result must be below the MRL.

12.3.3 In addition to analysis replicates that may be required to obtain the sample result, one sample per service request must be analyzed in duplicate or one per 20 samples, whichever is more frequent. The percent RPD for the duplicates must be **≤17%**. This statistically derived acceptance limit is subject to change as limits are updated. For SM 5310C, all duplicates must be within **10%** RPD.

Relative Percent Difference calculation:

$$RPD = \frac{(S - D)}{((S + D)/2)} \; X \; 100$$

where: S = Initial sample result
D = Duplicate sample result

12.3.4 Matrix Spikes- One spike sample must be analyzed per service request or one per 20 samples, whichever is more frequent. Spike 50 ul of 5000 ppm KHP stock solution to 10.0 mls of sample. For low level analysis, spike 50 ul of 1000 ppm KHP stock solution to 10.0 mls of sample. The matrix spike recovery must be **68-132%**. This statistically derived acceptance limit is subject to change as limits are updated.

Note: Method 9060 requires spike and spike duplicate be analyzed every ten samples.

Calculate percent recovery as follows:

$$Matrix\ Spike\ Recovery = \frac{Spiked\ Sample - Sample}{Spike\ Added} \times 100$$

13 DATA REDUCTION, REVIEW, AND REPORTING

Refer to the SOP for *Data Reporting and Report Generation* for reporting guidelines.

13.1 Preliminary results are reviewed to determine if dilutions are required. Sample information is transferred to an Excel spreadsheet for calculations (see R:\WET\ANALYSES\TOC\DATA). Instrument baseline is determined by taking the average of all Method Blanks, CCB's, and Reagent Blanks (see R:\WET\ANALYSES\TOC\TOC_CBA_LCS.XLS). Sample concentration is corrected by subtracting calculated blank average (CBA) from instrument response. Concentration and sample identification number are highlighted for reporting purposes.

13.2 For 5310C, report the result from a single analysis. For 9060A, report both the average and the range from the quadruplicate analyses.

13.3 It is the operators' responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 11 of SOP. Average, RPD, spike level and spike recovery are entered in spreadsheet (see append. B) for corresponding samples. All data will be initialed, dated and attached to required data quality worksheet.

13.4 Reports are generated in the CAS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). This compilation is then transferred to a file which Excel© uses to generate a report. The forms generated may be CAS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.5 As an alternative, reports are generated using Excel© templates located in R:\WET\FORMS. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The results are then transferred, by hand or electronically, to the templates the saved to R:\WET\WIP.

13.6 Data Review and Assessment

13.6.1 Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed.

Refer to the *SOP for Laboratory Data Review Process* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative.

14 CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements.

15 METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

The method detection limit (MDL) is established using the procedure described in the SOP *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual.

16 POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

17 WASTE MANAGEMENT

The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

18 TRAINING

18.1 Refer to the SOP for Documentation of Training for standard procedures.

18.2 Training outline

18.2.1 Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.2.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.2.3 Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.3 Training is documented following the SOP for Documentation of Training.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

19 CHANGES SINCE THE LAST REVISION

19.1 Removed reference to 415.1 a deleted method
19.2 Sec 1.2 & 1.4 are new.
19.3 Sec 6.6 is new.
19.4 Sec 11.3.3 is new.
19.5 Sec 12 re-formatted and expanded.
19.6 Sec 12.3 has been expanded.
19.7 Sec 13 expanded.
19.8 Sec 15 updated SOP reference.
19.9 Sec 20 updated references.

20 REFERENCES

U.S. Environmental Protection Agency, *Total Organic Carbon, Method 9060A,* Revision 1 November 2004

Total Organic Carbon, Combustion-Infrared Method, 5310C. Standard Methods for the Examination of Water and Wastewater, 20th ed., 1998.

APPENDIX A

Seawater, Brine, and High Chloride Samples

High levels of chloride ion present analytical problems not adequately addressed by EPA /9060. The major interferences associated with the analysis of seawater are overcome by maintaining effective Sample: Oxidant ratios, and allowing sufficient analysis time.

Chloride ions compete directly with carbon for available persulfate ions. In seawater and brine, the amount of chloride present in a sample is much greater than the organic carbon present. In these cases the recovery of TOC will suffer due to incomplete oxidation. Some precautions that can be taken are to increase reaction time and increase the volume and concentration (250g/L) of the persulfate reagent used during analysis. An increase in persulfate to 400 µL/sample will provide enough persulfate so that the organic carbon is able to oxidize.

The oxidation process of organic compounds by persulfate generally follows first order reaction kinetics. The oxidation of chloride to chlorine introduces intermediate steps, which result in a more complex reaction. This reaction proceeds more slowly. By extending the reaction time to 5 minutes, the reaction will have time to finish, resulting in complete oxidation of all the organic carbon present in the sample.

In addition to the modifications designed to eliminate chloride interferences, the instrument is configured to operate in a fashion that allows TIC to be vented during an extended purge period, thus avoiding I.R. saturation.

Consult user manual for more information pertaining to difficult sample matrices (Model 700, pg. 92 or Model 1010 pg. 77).

APPENDIX B

The calibration is determined using a linear regression that best fits the line of the X:Y pairs. The quality of the fit is determined by calculating the coefficient of determination (R^2), also called the correlation coefficient.

The line of regression is calculated as follows:

Start with the equation for a line, y = mx + b. From here the line of regression can be determined.

$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

Where:

x = the value of the x variable.
y = the value of the y variable.
n = the number of data points.

Once the line of regression has been determined then the coefficient of determination can be calculated.

$$r^2 = \frac{\left(\sum xy - n\bar{x}\bar{y}\right)^2}{\left(\sum x^2 - \bar{x}\sum x\right) * \left(\sum y^2 - \bar{y}\sum y\right)}$$

Attachment A

Analysis Benchsheet

COLUMBIA ANALYTICAL SERVICES, INC.

Matrix: WATER

Analysis: Total Organic Carbon (WATER) Method:Oxidation EPA 415.1/9060/5310C

Printout	Sample #	Dil. Factor	Solution Conc. ,mg/L	Blank Correction, mg/L	Net mg/L	TOC mg/L	Reported TOC mg/L	
CBA	RB	1			0.0000	0	<0.5	
2	ICV	1		0.0000	0.0000	0	<0.5	
3	ICB	1		0.0000	0.0000	0	<0.5	
4	CCV1	1		0.0000	0.0000	0	<0.5	
5	CCB1	1		0.0000	0.0000	0	<0.5	
6	MB1	1		0.0000	0.0000	0	<0.5	
7	LCS1	1		0.0000	0.0000	0	<0.5	
8		1		0.0000	0.0000	0	<0.5	
9		1		0.0000	0.0000	0	<0.5	
10		1		0.0000	0.0000	0	<0.5	
11		1		0.0000	0.0000	0	<0.5	
12		1		0.0000	0.0000	0	<0.5	
13		1		0.0000	0.0000	0	<0.5	
14		1		0.0000	0.0000	0	<0.5	
15		1		0.0000	0.0000	0	<0.5	
16	CCV2	1		0.0000	0.0000	0	<0.5	
17	CCB2	1		0.0000	0.0000	0	<0.5	
18		1		0.0000	0.0000	0	<0.5	
19		1		0.0000	0.0000	0	<0.5	
20		1		0.0000	0.0000	0	<0.5	
21		1		0.0000	0.0000	0	<0.5	
22		1		0.0000	0.0000	0	<0.5	
23		1		0.0000	0.0000	0	<0.5	
24		1		0.0000	0.0000	0	<0.5	
25		1		0.0000	0.0000	0	<0.5	

ICV = 20.0 (Ref.#TOC1-57-J) ICAL Date 8/01/08 ICAL ID#:TOC/1-96-N

LCS =24.7 ppm APG 4013 Lot #125384 (REF#TOC1-08-R)

CCV = 25.0 (Ref.#TOC1-47-S)

Spike: 0.05 ml of 5000 ppm stock ---> 10.0 mls =25.0 x Dilution Factor (Ref.# TOC1-22-C)

date time

Analyzed By:	Date Analyzed
Reviewed By:	Date Reviewed

COLUMBIA ANALYTICAL SERVICES, INC.

Matrix: WATER

Analysis: Total Organic Carbon (WATER) Method:Oxidation EPA 415.1/9060/5310C

Printout	Sample #	Dil. Factor	Solution Conc. ,mg/L	Blank Correction, mg/L	Net mg/L	TOC mg/L	Reported TOC mg/L	
CBA	RB	1			0.0000	0	<0.1	
2	ICV	1		0.0000	0.0000	0	<0.1	
3	ICB	1		0.0000	0.0000	0	<0.1	
4	CCV1	1		0.0000	0.0000	0	<0.1	
5	CCB1	1		0.0000	0.0000	0	<0.1	
6	MB1	1		0.0000	0.0000	0	<0.1	
7	LCS1	1		0.0000	0.0000	0	<0.1	
8		1		0.0000	0.0000	0	<0.1	
9		1		0.0000	0.0000	0	<0.1	
10		1		0.0000	0.0000	0	<0.1	
11		1		0.0000	0.0000	0	<0.1	
12		1		0.0000	0.0000	0	<0.1	
13		1		0.0000	0.0000	0	<0.1	
14		1		0.0000	0.0000	0	<0.1	
15		1		0.0000	0.0000	0	<0.1	
16	CCV2	1		0.0000	0.0000	0	<0.1	
17	CCB2	1		0.0000	0.0000	0	<0.1	
18		1		0.0000	0.0000	0	<0.1	
19		1		0.0000	0.0000	0	<0.1	
20		1		0.0000	0.0000	0	<0.1	
21		1		0.0000	0.0000	0	<0.1	
22		1		0.0000	0.0000	0	<0.1	
23		1		0.0000	0.0000	0	<0.1	
24		1		0.0000	0.0000	0	<0.1	
25		1		0.0000	0.0000	0	<0.1	

ICV = 4.00 (Ref.#TOC1-57-) ICAL Date 8/01/08 ICAL ID#:TOC/1-96-N

LCS =4.94 ppm APG 4013 Lot #125384 (REF#TOC1-08-)

CCV = 5.00 (Ref.#TOC1-62-)

100ppm Working Standard: 2.000ml of 5000ppm stock (REF#TOC1-22-B) ---> 50ml T.V. DI water (REF#TOC1-25-D)

date time

Analyzed By:	Date Analyzed
Reviewed By:	Date Reviewed

STANDARD OPERATING PROCEDURE

for

Sample Preparation for Particulate Carbon and Nitrogen and Particulate Organic Carbon in Water by Combustion / Thermo-Conductivity or Infrared Detection

SOP Code: GEN- PC PN POC PREP
Revision: .01

DATE: 7/3/09

Approved by: _____ _____
Ralph V. Poulsen, Laboratory Manager **Date**

_____ _____
Mary Tyer, Quality Assurance Program Manager **Date**

_____ _____
Kevin Mac Donald, Analyst **Date**

Columbia Analytical Services, Inc. – Tucson Laboratory
3860 S. Palo Verde Rd, Suite 302
Tucson, AZ 85714

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Effect. Date: _____
Initials: _____ Effect. Date: _____
Initials: _____ Effect. Date: _____

DOCUMENT CONTROL

NUMBER: GEN-PC PN POC PREP RV1
Effective
Initials: _____ Date: _____

Standard Operating Procedure
for
Sample Preparation for Particulate Carbon and Nitrogen and Particulate Organic Carbon in Water
by
Combustion / Thermo-Conductivity or Infrared Detection

1.0 SCOPE AND APPLICATION

1.1 Particulate Carbon (PC) and Particulate Nitrogen (PN) in the sediment fraction of water are determined by first separating the sediment from the water through filtration using glass fiber filters. PC and PN are then determined concurrently using a CHN elemental analyzer. PC can also be determined using a carbon elemental analyzer. A Perkin Elmer model 2400 or LECO Micro Truspec CHN analyzers are used for this analysis. An Eltra CS500 Carbon - Sulfur analyzer can also be used if PN is not required.

1.2 Particulate Organic Carbon (POC) is determined using this method by exposing the sediment on the filter to fuming HCl and then analyzing the filter for total carbon. This treatment step removes inorganic forms of carbon (carbonates) leaving the organic carbon on the filter.

1.3 The method detection limits for PC, POC, and PN are approximately 10 ug/L for PN or 50 ug/L for PC and POC based on analyzing a 200 mL water sample. Smaller or larger volumes of water can be filtered depending on the amount of sediment in the sample

.

1.4 The filtrate collected from the filtering process can be analyzed for Dissolved Organic Carbon (DOC) after the filtrate is preserved to a pH of <2 with concentrated Sulfuric Acid.

2.0 SUMMARY OF METHOD

A water sample is filtered through a pre-combusted and pre-weighed GF/F glass fiber filter to remove sediment from the water. The filter with sediment is dried and then re-weighed to determine the concentration of sediment in the water sample. The filter containing the sediment is analyzed by an elemental CHN or Carbon analyzer. These instruments employ direct combustion of the sample in ultra-pure oxygen at 935°C to 1350°C depending on instrument used. The elements of interest are converted to gases by the combustion process. Carbon is converted to CO_2 and nitrogen to NOx which is then reduced to N_2 and reported as PC or PN.

POC is analyzed using the same analytical technique by analyzing GF/F filters that have been treated with fuming HCl after filtering sediment from the water sample.

After performing the preparation of water samples using the procedures detailed in the SOP, the analyses are performed for PC, PN, and/or POC following procedures detailed in the appropriate SOPs for CHN or Total Carbon analyses.

3.0 DEFINITIONS

3.1 Analytical Protocol: Samples are analyzed in a set referred to as an analytical protocol or sequence. The protocol begins with instrument calibration followed by calibration verification, samples, and batch QC samples. The instrument calibration must be verified at a method-required frequency by the analysis of verification standards. The sequence ends when the set of samples has been analyzed and continuing calibration has been demonstrated. As long as the continuing calibration criteria are met, analysis may continue to proceed.

3.2 Benchsheet: A form used to record the analytical protocol, sample information, and data.

3.3 DI Water: DI Water is laboratory pure water that has been passed through an initial deionizing system followed by a polishing deionizing system (ultra-pure or nanopure) producing water that meets ASTM Type I criteria.

3.4 Prep Blank (PB): The prep blank for this method consists of analyzing a blank GF/F filter that has gone through the sample treatment procedure as the samples. The purpose of the PB is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples.

3.5 Organic Analytical Standard (OAS): These are analytically pure single compounds that are purified by multiple re-crystallizations or fine cut distillation in the case of OAS benzene. These standards are available from Exeter Analytical or other micro-elemental supplier and must be NIST traceable.

3.6 Laboratory Control Sample/Duplicate Laboratory Control Sample (LCS/LCSD): A LCS is a QC sample with known concentrations of analytes that is of the same matrix of the samples being analyzed. It is typically purchased from a qualified vendor and is supplied with certified true values and statistical acceptance ranges. The LCS may be a chemical, natural sample, or spiked natural matrix. Another name for LCS is Standard Reference Material (SRM) or Quality Control Sample (QCS).

3.7 Laboratory Fortified Blank (LFB): A LFB is a QC sample with known concentrations of analytes. It is prepared by analyzing an OAS (2 to3 mg of Acetanilide) in a tin capsule for Total C and Total N or 2 to 3 mg on a glass fiber filter for PC and PC.

4.0 INTERFERENCES

4.1 Samples with suspended sediment or organic material that is larger than 0.5 mm need to be homogenized using a blender in order to obtain a representative sample on the filter.

4.2 POC values may exhibit a high bias for samples with high concentration of sediments containing high levels of carbonates that do not fully react during the fuming HCl pretreatment step. A more aggressive acid treatment may be required in these situations.

5.0 SAFETY

5.1 Follow all CAS safety practices as described in the CAS Safety Manual.

5.2 The toxicity or carcinogenicity of each compound or reagent used in the method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to the compounds should be reduced to the lowest possible level. A reference file of material safety data sheets is available to all personnel involved in these analyses. Columbia Analytical Services also maintains a file of OSHA regulations regarding the safe handling of chemicals specified in these procedures.

6.0 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1 Environmental samples can be adversely affected by biological activity and must be collected, preserved, and analyzed in accordance with EPA method 440.0, "Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis".

6.1.1 Water samples are collected in clean amber glass bottles for Particulate Carbon (PC), Particulate Nitrogen (PN), or Particulate Organic Carbon (POC). The sample should be filtered through pre-combusted (550°C for 1.5 hr), pre-weighed GF/F glass fiber filters immediately after collection.

6.1.2 Used filters are stored at -20°C or can be dried at 103-105°C for 24 hr and placed in a desiccator.

6.1.3 A minimum of 2 filters and preferably three or four filters are needed for each sample.

6.1.4 If the water sample can not be filtered immediately, then the sample must be stored at 4°C.

6.2 There are no established holding times for this method. Samples should be handled as detailed above to avoid degradation of the samples.

7.0 APPARATUS AND EQUIPMENT

7.1 Oven, 103-105°C

7.2 Box Furnace, 550°C

7.3 Blender, glass or stainless steel

7.4 GF/F Glass Fiber Filters (47 mm and 25 mm)

7.5 Analytical Balance, 0.1 mg

7.6 Stainless steel fine tip forceps

7.7 Glass petri dish with lid, 60 x 15 mm

7.8 Porcelain dish, 100 mm

7.9 Vacuum Pump at < 10 in Hg

7.10 HCl Reaction Chamber, polypropylene box with lid and raised mesh floor

7.11 Refrigerator, 4°C

7.12 Freezer, -20°C

8.0 STANDARDS AND REAGENTS

8.1 Acetanilide, OAS 99.9% + purity

8.2 Hydrochloric Acid (HCl), Concentrated, ACS Reagent grade

8.3 Sulfuric Acid (H_2SO_4), Concentrated, ACS Reagent grade

9.0 PREVENTIVE MAINTENANCE

General preventive maintenance is required of support equipment used in this method. Follow the equipment manual for operation and preventive maintenance.

10.0 RESPONSIBILITIES

10.1 This SOP is intended for the use of experienced analysts. It should also be used for training of technicians and chemists in the above referenced method and as a reference for data reviewers for data generated by use of this SOP.

10.2 **Analyst:** The analyst is responsible for

- Performing the analysis according to the instrument manual, the method SOP, QA/QC criteria, and company safety procedures
- Properly operating and/or maintaining the instrument
- Entering the appropriate information onto the benchsheets and/or logbooks
- Documenting and notifying the laboratory director of any operational problems or failed QC data

10.3 **Laboratory Director:** The laboratory director or his/her assignee is responsible for:

- Training, scheduling, and supervising the performance of the CHN analyzer
- Reviewing and approving CHN QC and sample data, benchsheets, and logbooks
- Reviewing the final CHN data reported on the Certification of Analysis report
- Reviewing and maintaining the SOP for this method

11.0 PROCEDURE

11.1 Filtration of Water Samples for PC and PN Determination

11.1.1 Record samples to be tested on a Total Solids / Total Volatile Solids benchsheet form (see Attachment A). Each sample will use two to four filters.. List each filter on the benchsheet.

11.1.2 Place 47 mm GF/F Whatman glass fiber filters (25 mm if C & N is required or use of LL CE440 CHN analyzer required) in a clean porcelain dish and heat at 550°C in a furnace for 1.5 hours. Filters can be stacked.

11.1.3 Remove the porcelain dish with filters from the furnace and allow cooling for ~ 30 minutes. Place each pre-combusted filter in a labeled glass petri dish with cover and then store in a desiccator for a minimum of 60 minutes.

11.1.4 Weigh pre-combusted filter to 0.1 mg on analytical balance, record weight, and return filter to petri disk and cover with lid. (Note - Use flat nose Teflon tip forceps when handling the filters)

11.1.5 Set up filtration rack with pre-cleaned 2 L filtering flasks and magnetic filtering funnels.

11.1.6 Assemble filtering funnel with first pre-weighed filter. Place filtering funnel into filtering flask.

11.1.7 Thoroughly mix the sample in the 1 L amber bottle and pour off 200 mL of sample into a pre-cleaned 200 mL Class A graduated cylinder. Larger or smaller volumes of sample can be used depending on the amount of sediment in the water and the desired detection limit. If the sample contains coarse organic matter, blend the sample in a glass or stainless steel high speed blender until the particles are < 0.5 mm in size.

11.1.8 Apply vacuum (at < 10 in Hg) to filtration unit and pour 50 mL aliquots of sample into the filtering funnel until the entire 200 mL is filtered. Gently swirl the last 50 mL aliquot in the graduated cylinder to re-suspend any sediment that has dropped out. Make sure that all sediment is transferred to the filtering funnel. If necessary use some of the filtered sample to rinse any remaining sediment from the cylinder into the filtering funnel or any sediment that may be adhering to the side of the filtering funnel down to the filter. Continue to apply vacuum until the GF/F filter is air dried. NOTE - Do not rinse the graduated cylinder, filtering funnel or filters with deionized water.

11.1.9 Turn off vacuum and carefully remove the filter and place in the appropriate petri dish and cover with lid.

11.1.10 Repeat steps 6 through 9 one to three more times for a total of 2 to 4 filters for each 1 L sample. Collect the filtrate in the original 2 L filtering flask for all 200 mL fractions.

11.1.11 After completing the filtration steps for the all 200 mL aliquots, discard the remaining sample in the original 1 L amber bottle. Rinse the 1 L amber bottle with several small aliquots of filtered sample discarding the rinses. Pour the remaining filtered sample into the rinsed 1 L amber bottle. If the 1 L amber bottle can not be rinsed clean, use a new bottle. Preserve the filtered sample with 2 mL of concentrated H_2SO_4 and mark with appropriate label. This sample can be used for Dissolved Organic Carbon.

11.1.12 Place petri dish and filter with lid removed in an oven at 103 to 105°C for 24 hours. Repeat drying cycles are 1 hour.

11.1.13 Remove petri dish and filter from oven, cover with lid, and place petri dish in a desiccator for at least 30 minutes.

11.1.14 Remove petri dish and filter from desiccator and weigh filter and record weight to nearest 0.1 mg taking care to not lose any sediment on the filter.

11.1.15 Return filter to petri dish and then to oven and repeat steps 12 through 14 drying the sample for one hour. Record second dry weight of filter on benchsheet. Repeat steps 12 through 14 if the difference between the initial and second weighing of the dried filter is greater than 0.6 mg or if the sediment on the filter weighs 12.5 mg or more, repeat the drying and re-weighing steps if the difference between the weights of the filter is > 4% of the mass of the sediment.

11.1.16 Record the weights of the filter and volume of sample used on the benchsheet and calculate the concentration of sediment in the sample in mg/L for each filter. The filters are now ready for analysis for PC and/or PN or for pre-treatment for POC.

11.2 Fuming HCl Treatment for POC Determination

11.2.1 **NOTE – all of the following steps must be conducted in a fume hood to prevent exposure to HCl fumes. Proper personal protection gear including lab coat, safety glasses, and gloves must be worn**.

11.2.2 Prepare the HCl reaction chamber (polypropylene box with lid and raised mesh floor) by pouring 100 mL of concentrated HCl in the bottom of the chamber. Place the raised floor in the chamber making sure that it is above the HCl.

11.2.3 Remove the lids from the petri dishes and place petri dishes with the filters on the raised floor of the reaction chamber. Close the chamber and leave the samples in the chamber undisturbed for 24 hours.

11.2.4 At the end of 24 hours, remove the petri dishes and cover them with their lids. Wipe the outside of the petri dishes with a damp paper towel to remove any HCl residue. The samples are now ready to analyze for POC.

12.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

12.1 **Preparation Blank:** Analyze one PB in ten or less samples. All PBs must have C or N values less than 0.025 mg/L (based on a 200 mL sample) or less then 10% of the PC, POC, or PN concentration in the samples.

12.2 **Laboratory Control Sample:** Analyze one LCS in ten or less samples. All LCSs must have recoveries of 95% to 105% or within the manufacturer's control limits if they are greater than the 95% to 105% range.

12.3 **Duplicate Analyses:** Analyze one duplicate in ten or less samples. The Relative Percent Difference (RPD) for analyses should be less than 20% provided the analyte concentration is > 10 times the RL.

12.4 **Laboratory Fortified Blank:** Analyze one LBF in ten or less samples. All LFBs must have recoveries of 85% to 115%.

12.5 Any deviations of the QA/QC requirements must be documented on the benchsheet and the Laboratory Supervisor or his/her designate notified prior to submitting data for approval.

13.0 CALCULATIONS, DATA REDUCTION AND REPORTING

13.1 **Calculations:**

13.1.1 Use the equation below to calculate the RPD.

$$RPD = \frac{S-SD}{AVG} * 100$$

Where:

S = *Sample result*
SD = *Sample duplicate result*
AVG = *Average of S and SD*

13.1.2 Use the equation below to calculate the % Recovery.

$$R = \frac{OV}{TV} * 100$$

Where:

OV = *Observed value*
TV = *True Value*

13.2 Validation:

The data acquired for a sample must be reviewed and validated against the quality control data acquired during the analysis. The following list of items must be checked and verified to meet acceptance criteria before approval for reporting of PC, PN, or POC results:

- Calibration Verification Standards meet criteria
- Preparation Blanks meet criteria
- LCSs meet criteria
- Duplicate Analyses meet criteria.
- Laboratory Fortified Blanks meet criteria
- All dilutions included in sample result calculations

13.3 Documentation

13.3.1 Record the start time and finish time and temperatures of the furnace and oven in their respective logbooks.

13.3.2 Record the calibration verification of the balance in its logbook.

13.3.2 Record the information detailed on the benchsheet (see attached example)

13.4 SOP Annual Review

13.4.1 This SOP must be reviewed at least once a year to determine if any changes are required. This review is performed by the laboratory director, laboratory supervisor, analyst performing the method, and the QA office.

13.4.2 If changes are required then a new revision is prepared and issued according to ADM-SOP.

13.4.3 If no changes are required then each applicable person must document that this SOP has been reviewed on the front page of this SOP. A memo stating that the SOP has been reviewed and is still in effect issued by the appropriate Supervisor.

14.0 METHOD PERFORMANCE

14.1 Reporting Limit

The Reporting Limit (RL) for PC, PN, and POC is dependent on the volume of sample filtered. The RLs for PC, PN, and POC are calculated using a RL 0.05 wt% from Total Carbon and Total Nitrogen (based on a 10 mg sample) using the following equation:

*PC, PN, or POC mg/L = 0.05 wt% * 10,000 * 0.01 g / Sample Volume mL*

For a 200 mL sample the Reporting Limit for PC, PN, or POC is 0.025 mg/L.

14.2 Method Detection Limit

For data to be reported to the MDL, determine the MDL using the following procedure.

14.2.1 MDL studies for PC, PN, and POC samples are conducted by analyzing 7 or more replicates of a low level LCS or SRM that is approximately 5 times higher than the historical MDL. Several different LCSs or SRMs may be required to meet the 5X rule for all of the analytes.

14.2.2 The MDL is calculated by multiplying the standard deviation by the Student's t value for n-1 degrees of freedom at the 99% confidence level (3.143 for 7 replicates).

14.3 Initial Demonstration of Capability

Before analyzing client samples for reporting purposes, the analyst must analyze four sample/sample duplicate pairs.

14.3.1 Analyze four LCSs.

14.3.2 After analysis is completed, calculate Recovery. The recoveries of the four LCSs must be 95% – 105%.

14.4 Practical Range

The practical range for this method is 0.025 mg/L to 100 wt% depending on the concentration of sediment in the water sample.

14.5 Precision and Accuracy

See **Section 12**.

15.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

15.2 The laboratory will comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the laboratory Safety Manual.

16.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

16.1 Corrective Action:

The corrective action process is initiated when data quality problems are observed or suspected. These cases include contamination of blanks, RPD or recovery outside of Laboratory established limits, exceeded sample holding time, etc.

16.2 Method Blank:

Method Blank contamination indicates the potential for a positive bias in the sample data. The MB should be re-analyzed using a new optical cell. If this solves the problem then the previous cell is considered too worn or scratched and should be discarded. Re-prepare all samples for which the result is less than 10 times the level detected in the MB. If reanalysis is not possible, flag the sample data as an estimated value in the analytical report.

16.3 Relative Percent Difference:

If the relative percent difference in the matrix sample/sample duplicate does not meet acceptance criteria, check sample for homogeneity. If the sample duplicate is outside of the RPD acceptance range repeat analysis.

16.4 Nonconformity Documentation:

Out of control events, conditions adverse to quality, are reported, documented and corrected. Out of control events (OOCE) may arise from the failure of a process, human error, non-compliance with requirements, inadequate controls, or sample matrix problems.

16.4.1 Data quality issues must be documented on the analytical raw data and/or the data review checklist. All appropriate data qualifiers must be added to the final reported results.

16.4.2 Problems that arise from actions under laboratory control (e.g. blank contamination, blank spike failure), affect more than one batch, are more serious in nature, or are indicative of an ongoing problem are documented on a Nonconformity and Corrective Action Form (NCAR).

16.4.3 **Appendix B** contains copies of the NCAR. It is filled out by the person identifying the event. Corrective action may require consultation with the Department Manager, the QA Manager, and the Laboratory Director. The corrective action is then approved by the Supervisor and/or section Manager. The QA Manager gives final approval, and if necessary, provides to Project Chemists(s) for client notification. A copy of the form is kept with the raw data, in the project file, and the original is filed in the QA file.

17.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Any event that arises and does not conform to what is expected either by the instrument or the QC generated. An NCAR must be filled out in order to document the corrective action measures taken. In addition, the Laboratory Manager and/or the individual Project Chemists must be notified.

18.0 REFERENCES

18.1 EPA, *Method 440.0 – Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis*, Rev. 1.4, September 1997

18.2 Columbia Analytical Services, Tucson, Arizona , *Standard Operating Procedure for CHN by Combustion / Thermo-Conductivity Detection,* most current version.

18.3 Columbia Analytical Services, Tucson, Arizona , *Standard Operating Procedure for Carbon and Sulfur by Combustion / IR Detection,* most current version.

19.0 TRAINING PLAN

19.1 Review literature (see references Section 18). Review the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

19.2 The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from assisting, to performing the procedure with minimal oversight from the experienced analyst.

19.3 Perform the initial precision and recovery (IPR) study, or initial demonstration of capability (IDC). Summaries of the studies are reviewed and signed by the supervisor and quality assurance program manager. Copies are maintained in the employee's training file.

20.0 METHOD MODIFICATIONS

None

21.0 INSTRUMENT-SPECIFIC ADDENDUM

None

22.0 CHANGES FROM PREVIOUS REVISION

None – new SOP.

ATTACHMENTS

23.1 **Appendix A** – Example Total Solids / Total Volatile Solids benchsheet

23.2 **Appendix B** - Form for documenting nonconformity

Appendix A

Example Total Solids / Total Volatile Solids Benchsheet

Columbia Analytical Services - Tucson, AZ

Total, Fixed, and Volatile Solids in Water, Solids, and Biosolids

EPA 1684, Gravimetric, 105C & 550C

Analyst:
Analysis Date:
Analyst Review:
Supervisor Review:

Method of Drying	Temp °C	Start Time	End Time		Method of Ash	Temp °C	Start Time	End Time

SX Type	Reference Number	Cup No.	Sx Vol mL	Filter Wt. g	Filter & Dry Solids Wt.1 g	Filter & Dry Solids Wt.1 g	Filter & Ash Solids Wt.1 g	Filter & Ash Solids Wt.2 g	Total Solids wt%	Fixed Solids wt%	Total Volatile Solids wt%	Remarks

Page 1 of 1 Benchsheet - TS FS TVS in Water Sludges.xls, 7/5/2009

Appendix B
Example Form for Documenting Non-Conformance

Columbia Analytical Services

Nonconformity and Corrective Action Report

SAMPLES/SYSTEM/JOB/CLIENT AFFECTED N&CA Report No. 2008-_____

NONCONFORMITY

Analysis/Event: _____

Instrument/System: _____ Da_____

Detailed Description of Nonconformity:

Originator (name): _____ Date: _____

Supervisor Verification: _____ Date: _____

CORRECTIVE ACTION AND OUTCOME

Detailed Description: (Re-establishment of conformity must be demonstrated and documented. Describe the steps that were taken, or are planned to be taken, to correct the particular Nonconformity and prevent the reoccurrence of the Nonconformity.)

Is the data to be flagged in the Analytical Report with an appropriate qualifier? **No** **Yes**

Person Responsible: _____ Date: _____

Supervisor Verification: _____ Date: _____

NOTIFICATION - CUSTOMER/CLIENT - INTERNAL/EXTERNAL

Project Chemist Notified by: _____ Date: _____

Customer Notified? **No** **Yes** If Yes, Notifier: _____ Date: _____

Project Chemist/Customer Comments (Retain record, e.g. telephone record, e-mail) _____

_____

ACCEPTANCE OF CORRECTIVE ACTION

Comments:

Corrective Action(s) have been implemented. QA Pgm Mgr: _____ Date: _____

STANDARD OPERATING PROCEDURE

STANDARD TEST METHODS FOR DETERMINING SEDIMENT CONCENTRATION IN WATER SAMPLES

GEN-D3977

Revision 0

Approved By:

_____	Supervisor	7/11/11 Date
_____	QA Manager	7-11-11 Date
_____	Laboratory Director	7/11/11 Date

COLUMBIA ANALYTICAL SERVICES, INC.
1317 South 13th Avenue
Kelso, Washington 98626

DOCUMENT CONTROL	
NUMBER:	
Initials:	Date:

SEDIMENT CONCENTRATION IN WATER

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) describes the procedure used for the analysis of sediment concentrations in water and wastewater using Method ASTM D3977-97. This procedure describes both the preparation and analysis procedures used to determine the sediment concentration.

1.2. This procedure is used to determine suspended solids using ASTM Method D3977 – 97. The procedure tests for material in a well-mixed water and wastewater collected from industrial effluents and storm water outfalls, lakes, streams and other water bodies. .

1.3. The Method Reporting Limit (MRL) is a function of the sample volume used and range of the balance.

2. METHOD SUMMARY

2.1. This procedure describes three different procedures to determine the sediment concentration: Evaporation, Filtration and Wet-Sieving – Filtration.

2.2. Test Method A – Evaporation can be used only on sediments that settle under the influence of gravity. Sediments are allowed to settle within the allotted storage time of the samples which usually ranges from a few days to a few weeks. After the sediment has settled, most of the supernatant water is pored off. The volume of water-sediment mixture remaining is measured so that a dissolved-solid correction can be applied. The sediment is then dried and weighed. Sediment concentration is then calculated.

2.3. Test Method B - Filtration is used only on samples containing sand concentrations less than about 10,000 ppm and clay concentrations less than about 200 ppm. The sediment need not be settleable because filters are used to separate water from the sediment. Correction factors for dissolved solids are not required. The sample is weighed and then filtered through a glass-fiber disk. The disk and sediment are dried and weighed, and then the sediment concentration is calculated.

2.4. Test Method C - Wet-Sieving-Filtration is used if two concentration values are required: one for sand-size particles and one for the combination of silt and clay-size particles. The silt-clay fraction need not be settleable. The sample is purred onto a 62 – 63 um sieve. The entire coarse fraction is used a

2.5. The practical range of determination is 5 mg/L to 20,000 mg/L if a 200 mL sample is used. The practical range of determination is 1 mg/L with 1000 mL of sample.

3. **DEFINITION**

3.1. Dissolved solids-soluble constituents in water. The quantity is determined by evaporating a water sample to visible dryness at a temperature slightly below boiling. The temperature is then raised to 105°C and held for about 2 h. This is followed by cooling in a desiccator and weighing the residue.

3.2. Fluvial sediment-particles that are (a) derived from rocks or biological materials and (b) transported by flowing water.

3.3. Sediment concentration-(a) the ratio of the mass of dry sediment in a water-sediment mixture to the mass of the mixture or (b) the ratio of the mass of dry sediment in a water sediment mixture to the volume of mixture.

3.4. Supernatant-clear overlying liquid in a sediment sample

3.5. Suspended sediment-sediment supported by turbulent currents in flowing water or by Brownian movement.

3.6. Total suspended solids, also known as non-filterable residue, is defined as those solids which are retained by a glass fiber filter and dried to a constant weight at 103-105°C.

3.7. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8. Laboratory Control Samples (LCS) – The LCS is a aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

4. INTERFERENCES

4.1. Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded if it is determined that their inclusion is not desired in the final result.

4.2. Using test Method B, excessive residue on the filter may form a water-entrapping crust. Limit the sample size to that yielding no more than 200 mg residue.

4.3. For samples high in total dissolved solids, thoroughly wash the filter to ensure removal of dissolved material.

4.4. Prolonged filtration times resulting from filter clogging may produce high results because of increased colloidal materials captured on the clogged filter.

4.5. Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because they can affect the results.

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and the MSDS where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

6. SAMPLE COLLECTION, CONTAINERS, AND STORAGE

6.1. Any type of container, glass or plastic, can be used.

6.2. Samples are non-preserved and kept at 4 ± 2°C until analysis to minimize decomposition of solids. The analysis holding time is 14 days.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

7.1.2. Reagent water - ASTM Type II de-ionized water. Reagent water must be interference free.

7.2. Standards

7.2.1. Stock standard solutions may be purchased from a number of vendors. All standards purchased from vendors must be traceable to NIST or A2LA certified reference materials. Purchased standards are prepared in DI water. The vendor-assigned expiration dates is used.

7.2.2. Laboratory Control Sample (LCS) – Prepared form ERA, QC Plus-solids, and Catalog No. 4033.

7.2.2.1. The LCS is prepared by transferring a container of QC Plus – Solids, to 1000 mL volumetric flask. This is done by wetting the contents of the vial with about 2 mL of DI water and transferring the wetted solids standard to a 1000 mL volumetric flask to which 100 – 200 mL of DI water has been previously added. Rinse the standards container 3 times with DI water to ensure all content are transferred to the volumetric flask. Bring up to 1000 mL in the volumetric flask with DI water

7.2.2.2. Document the preparation of the LCS solution in a reagent log book. The true values or concentrations of all units from the standards certificate of analysis. This standard is good for 7 days and is stored at 4 ± 2°C.

7.2.2.3. A low level LCS-LL solution is prepared by taking 200 mL of the LCS solution and bringing up to 1000 mL in a volumetric flask with DI water. This standard is good for 7 days and is stored at 4 ± 2°C.

8. APPARATUS AND EQUIPMENT

8.1. Glass fiber filter discs, 42.5 mm, Whatman GF/C

8.2. Evaporating Dishes or Beakers – Preweighted containers of porcelain or glass with capacities of about 150 mL.

8.3. Magnetic Filtration Apparatus

8.4. Suction Flask, 1 L

8.5. Glass petri dishes with tops for drying filters

8.6. Drying Oven and thermometer. The thermometer is immersed in sand, or other suitable solid material, in a flask in the oven.

8.7. Desiccator

8.8. Forceps

8.9. Graduated Cylinders

8.10. Analytical Balance, capable of weighing to 0.1 mg,

8.11. Balance calibration verification weights, ASTM Class 1; 1g, 10g, 100g

8.12. Eight inch Sieve with 62 or 63 um square aperatures.

8.13. Splitter, for extracting an aliquot of the mesh

9. PREVENTIVE MAINTENANCE

9.1. Oven thermometer calibration is performed quarterly by the QA staff. Multi-point balance calibration checks are performed daily for each day analysis are performed. The results of these checks are recorded in the appropriate logbook. See the SOP *Support Equipment Monitoring and Calibration (ADM-SEMC)* and *Laboratory Balance Monitoring and Calibration (ADM-BAL).*

9.2. Laboratory QA staff coordinates periodic outside service, calibration, and cleaning. Laboratory QA staff is responsible for reviewing and maintaining the outside service certificates.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. When samples arrive at the laboratory, group them according to sampling stations and then arrange each group in chronological order according to times of sample collection. Separate those samples to be analyzed for concentration from those to be analyzed for particle-size distribution or other properties. A data sheet should then be completed for each concentration sample.

11.2. Check each sample for: (1) loss of water caused by leakage or evaporation, (2) loss of sediment which is sometimes revealed by the presence of particles on the outside of the sample bottle, (3) accuracy of sample-identification notes, and (4) a container tare which is usually etched on the bottle. Enter all appropriate notes, observations, and data on the laboratory form.

11.3. Remove the bottle caps then weigh each container along with its water-sediment mixture to the nearest 0.5 g. Record each reading on the corresponding bottle and on the laboratory form.

11.4. Replace the caps then store the samples in a cool, dark place to minimize microbiological and algal growth. Inspect the bottles frequently; if the sediment does not settle within about 14 days use Test Method B (filtration procedure) for the analysis. If settling proceeds at an acceptably rapid rate, use Test Methods A, B, or C.

11.5. **TEST Method A – EVAPORATION**

11.5.1. This test method can be used only with sediments that settle under the influence of gravity. This test method is applicable to samples ranging from 0.2 to 20 L in volume, from 5 to 550000 mg/L in sediment concentration, and having less than 35,000 mg/L in dissolved- solid concentration.

11.5.2. After the sediment has settled, most of the supernatant water is poured or siphoned away. The volume of water-sediment mixture remaining is measured so that a dissolved-solids correction can be applied later. The sediment is then dried and weighed. Sediment concentration is calculated in accordance with section

11.5.3. After the sediment has settled, decant or vacuum away as much supernate as possible without disturbing the sediment. This can be accomplished by connecting a J-;haped plastic, copper, or glass tube to the vacuum line and lowering the tube until the curved section is near the bottom of the sample bottle. Supernate enters the upward-facing end of the tube and thereby flows away without creating currents

and eddies in the sediment layer. Save the supernate for a dissolved-solids correction factor to be determined later.

11.5.4. After decanting about 40 to 70 mL of water sediment mixture should be left. To determine the exact volume, place the sample bottle on level support then mark the liquid surface on the outside of the bottle. Use water to wash all of the sediment and supernate into an evaporating dish, then refill the sample bottle to the mark with water from a graduated cylinder. Record the volume added to the sample bottle.

11.5.5. Place the evaporating dish in the oven with the temperature set slightly below boiling. Maintain this temper-ature until all visible traces of water have evaporated. Then raise and hold the temperature at 105"C for about 2 h .

11.5.6. Transfer the dish from the oven to the desiccator; allow the sediment to cool to room temperature.

11.5.7. Weigh the dish to the nearest 0.0001 g as quickly as possible to minimize absorption of moisture from the air. Record the weight of the dish and its contents and also the tare weight of the dish on the laboratory form. Subtract the tare from the gross, then record the net weight.

11.5.8. For nearly all sediment samples, a single drying cycle is sufficient to obtain stable weight; however, a few samples, principally those containing high concentrations of organic materials, may have to be dried a second time. If weight shifts occur, the specimens should be dried and weighed a third time to verify that the weights are stable.

11.5.9. Determine the dissolved-solids correction factor by using a volumetric pipet to transfer an aliquot (measured volume) of supernatant into an evaporating dish. Record the aliquot volume.

11.5.10. Set the oven temperature slightly below the boiling point of water and evaporate the supernatant to visible dryness. Then raise and maintain the oven temperature at 105°C for at least 2 h. After this cool the dish in a desiccator. Then weigh the dish and its contents to the nearest 0.0001 g. Record this gross weight and also the tare weight of the dish on the form. Subtract the tare from the gross and record the net weight of dissolved solids in grams.

11.5.11. Calculation

11.5.12. Determine the dissolved-solids correction according to Eq 1:

DSc = (DS/Va) x Vs

where
DSc = dissolved-solids correction, g,
DS = net weight of dissolved solids, g,
Va = aliquot volume taken for dissolved solids, mL,
Vs = volume of supernate remaining with the sediment

11.5.13. In Eq 1, DS/Va is the concentration of dissolved solids in the supernatant (see 11.5.9). This concentration is multiplied by Vs to obtain the dissolved-solids weight in the dry sediment (see 11.5.7). Enter the value of DSc on the laboratory form under the heading D. S. Corr.

11.5.14. Subtract the value of DSc in 11.5.12 from the net weight determined in 11.5.7. Record the difference on the laboratory form under the second heading labeled Weight of Sediment-Net. Notice each laboratory form has two rows with this heading.

11.5.15. Divide the Net Weight of Sediment (second entry) by the Net Weight of Sample. Both weights must be in the same units, preferably grams. Multiply the quotient by one million, then enter the result under the heading Conc (ppm) on the laboratory form.

11.5.16. Modern practice calls for reporting sediment concen-trations in. milligrams per liter instead of ppm as determined in 11.5.15. Conversion can be made with the aid of Table 1. For example, consider a sediment concentration of 41,000 ppm. The multiplier obtained from Table 1 is 1.03; therefore, the concentration is 41000 x 1.03 = 42300 mg/L. The equation immediately following Table 1 can be used instead of the multipliers. Equation 1 is easier to use in computer programs and is applicable to concentrations beyond the range in the table.

TABLE 1: Factors for Conversion of Sediment Concentration in Parts per Million (ppm) to Grams per Cubic Meter (g/m3) or Milligrams per Liter (mg/L)

Range of Concentration 1000 ppm	Multiply By	Range of Concentration 10 000 ppm	Multiply By	Range of Concentration 100 000 ppm	Multiply By
0-7.95	1.00	153-165	1.11	362-380	1.30
8.0-23.7	1.01	166-178	1.12	381-398	1.32
23.8-39.1	1.02	179-191	1.13	399-416	1.34
39.2-54.3	1.03	192-209	1.14	417-434	1.36
54.4-69.2	1.04	210-233	1.16	435-451	1.38
69.3-83.7	1.05	234-256	1.18	452-467	1.40
83.8-97.9	1.06	257-278	1.20	468-483	1.42
98.0-111	1.07	279-300	1.22	484-498	1.44
112-125	1.08	301-321	1.24	499-513	1.46
126-139	1.09	322-341	1.26	514-528	1.48
140-152	1.10	342-361	1.28	529-542	1.50

11.6. **TEST METHOD B-FILTRATION**

11.6.1. Test Method B can be used only on samples containing sand concentrations less than about 10 000 ppm and clay concentrations less than about 200 ppm. The sediment need not be settleable because filters are used to separate water from the sediment. Correction factors for dissolved solids are not required.

11.6.2. Even though a high-concentration sample may filter slowly, users should not divide the sample and use two or more filters. Instead, the entire sample should be filtered through one disc.

11.6.3. Preparation of glass fiber filter disc - Place the disc on membrane filter apparatus. While vacuum is on, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings. Remove filter from the apparatus and place in a petri dish. Dry the filters in an oven at 103-105°C for one hour. Remove to a desiccator and cool for at least 30 minutes. Weigh immediately before use. Note: The filter should be handled with forceps at all times.

11.6.4. Selections of sample volume - For clean samples, choose a sample volume of 1000 mL. If during filtration of the initial volume, the filtration rate drops rapidly, or if

filtration time exceeds 5 to 10 minutes, the sample volume should be decreased. A smaller sample volume may be used initially if it is apparently visible that the TSS concentration will be high.

11.6.5. Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat the fritted support.

11.6.6. Shake the sample vigorously and transfer the predetermined sample volume selected to the filter using a graduated cylinder.

11.6.7. Filter the sample through the glass fiber filter.

11.6.8. With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

Note: Total volume of wash water used should equal approximately 30 ml.

11.6.9. Carefully remove the filter from the filter support. Dry overnight at 103-105°C. Cool in a desiccator and weigh to the nearest 0.0001 g.

11.6.10. Return the filters to the oven and dry at least one hour at 103-105oC. Cool in a desiccator and weigh. The weight must agree with the first weight, within 0.5 mg. If not, repeat dryings until weights agree within 0.5 mg.

11.6.11. **Instructions for 24 hour rush samples**

11.6.11.1. Dry at least one hour at 103-105oC. Samples high in suspended solids may need a longer drying period.

11.6.11.2. Cool in desiccator and weigh.

11.6.11.3. Repeat 11.6.11.1 and 11.6.11.2 until weights agree within 0.5 mg.

11.6.11.4. Record the balance I.D. used for all weightings on the bench sheet.

11.6.11.5. Calculate sediment concentration as follows:

$$\text{Sediment conc. mg/L} = \frac{(A-B) \times 1000}{\text{Sample volume, mL}}$$

Where: A = weight of dried residue + filter, mg, and
B = weight of pre-washed filter, mg.

11.7. **TEST METIIOD C-WET-SIEVING-FILTRATION**

11.7.1. This test method covers concentration measure-ments of two fractions. The term fine fraction refers to small enough to pass a sieve with 62 or 63 um apertures; coarse fraction refers to particles large enough to be retained on the sieve. The fine fraction need not be settleable. This test method is useful when large samples must be collected in the field but only small subsamples, typically 300 to 500 mL can be shipped back to the laboratory.

11.7.2. The sample is poured onto a sieve with 62 or 63 um openings. Analysis includes the entire coarse fraction but only a small, measured aliquot of the fine fraction. Sieving and aliquot extraction can be performed either at the sampling site or in the laboratory.

11.7.3. Measure the gross and tare weight of each sample and record the readings on the laboratory benchsheet.

11.7.4. Hold the sieve over a beaker or large, shallow dish. Pour the sample through the sieve. Some sediments may require vigorous rinsing with water to disaggregate clumps retained in the sieve. Use a minimum amount of and retain in the dish with the fine fraction.

11.7.5. Wash the coarse fraction from the sieve into a pre-weighed evaporating dish. Dry, desiccate, and weigh the sediment in accordance with section 11.5.5 through 11.5.7. Record the net weight of the coarse fraction.

11.7.6. If possible, the sample received at the laboratory should be analyzed in its entirety, but if the sample volume is unwieldy it may be reduced by splitting. Mix the fine fraction by vigorously shaking and stirring, then, without pausing; pour the mixture through the splitter and into a clean container.

11.7.7. Determine and record the net weight of the aliquot to the nearest 0.1 g and record on the benchsheet.

11.7.8. The aliquot is usually analyzed by the filtration method, but it can be analyzed by the evaporation method. If filtration is used, follow the procedure 11.6.3 through 11.6.6; if evaporation is used, follow the procedure in 11.5.3 through 11.5.10.

11.7.9. Calculation

11.7.9.1. Calculate the coarse-fraction concentration as:

$$C_{cf} = C \times 10^6 / S$$

Where:
C_{cf} = Coarse fraction concentration, ppm
C = mass of the sediment in the coarse fraction, g, and
S = mass of the entire sample, g.

11.7.9.2. Calculate the fine fraction concentration as:

$$C_{ff} = F \times 10^6 / W$$

C_{ff} = Fine fraction concentration, ppm
F = mass of the sediment in the aliquot, g, and
W = mass of the aliquot, g.

12. QUALITY CONTROL

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or when ever significant changes to the procedures have been made. To do this, four water samples are spiked with the LCS spike solution, then prepared and analyzed. Acceptance criteria are the same as LCS criterion.

12.2. Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). General QC Samples are:

12.2.1. Prior to, and after each analysis batch, balance calibration verification is performed using weights bracketing the sample weights. Balance calibration verification measured weights must be ± 0.5% of the true value.

12.2.2. Method Blank

12.2.2.1. A method blank is extracted and analyzed with every batch of 10 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows analytes above the reporting limit, corrective action must be taken. Corrective action include reclassification, reanalysis, system cleaning, or re-extraction and reanalysis.

12.2.3. Lab Control Sample (LCS)

12.2.3.1. The laboratory control sample is composed of analyte-free water or solid matrix (sodium sulfate or sand) into which is spiked a number of appropriate target analytes. The LCS is designed to monitor the accuracy of the procedure. The concentration of the spike in the LCS matrix should be at 5 to 10 times the MRL or at levels specified by a project analysis plan.

12.2.3.2. A lab control sample (LCS) must be prepared and analyzed with every batch of 20 (or fewer) samples. Calculate the LCS recovery as follows:

%R = X/TV X 100

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

12.2.3.3. The acceptance criterion is ± 15% of the true value. If the recovery is within control limits, the analysis is in control and results may be reported. If not, this indicates that the analysis is not in control. Samples associated with the 'out of control' LCS, shall be considered suspect and corrective action is taken. The samples are re-extracted or re-analyzed or the data reported with the appropriate qualifiers.

12.2.4. A sample duplicate is prepared and analyzed with every batch of ten sample or fewer samples.

12.2.4.1. Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{R1 - R2}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.2.5. Duplicates should have an RPD $\leq$ 10%.

13. DATA REDUCTION , REVIEW, AND REPORTING

13.1. Data Review and Assessment

13.1.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process (ADM-DREV)* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative.

13.2. Reporting

13.2.1. Refer to the SOP for *Data Reporting and Report Generation (ADM-RG)* for reporting guidelines.

13.2.2. The analyst enters data directly into CASLIMS templates. An Analytical Results Summary is generated for that analytical batch showing all QC and sample results. After primary and secondary review, final reports are generated in CASLIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). The forms generated may be CAS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.2.3. Report in mg/L Total Sediment concentration using whole numbers.

13.2.4. The Method Reporting Limit is 5 mg/L for 200 mL samples and 2 mg/L for 500 mL samples.

13.2.5. Significant Figures: Use up to a maximum of three significant figures.

13.2.6. Sample concentrations are reported when all QC criteria for the analysis has been met. Reported results not meeting QC criteria must be qualified with a standard CAS footnote.

14. CORRECTIVE ACTION

14.1. Refer to the SOP for Corrective Action (ADM-CA) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when:

- Corrective action is not taken or not possible
- Corrective action fails to correct an out-of-control problem on a laboratory QC or calibration analysis
- Reanalysis corrects the nonconformity but is not a procedurally compliant analysis

15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

16. POLLUTION PREVENTION

16.1. It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

18. TRAINING

18.1. Refer to the SOP for Documentation of Training. The SOP describes the training outline and necessary documentation.

18.2. Review literature (see References section). Review the SOP. Also review safety procedures. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.3. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 1-2 months. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

18.4. Independently perform Initial Demonstration of Proficiency studies and QC analyses. The data must be reviewed by a supervisor or trained analyst. Documentation is forwarded to the employee's training file.

19. REFERENCES

19.1. Standard Test Methods for Determining Sediment Concentration in Water Samples, ASTM D 3977 – 97, 1999 Annual Book of ASTM Standards, Vol. 11.02, p. 389 – 394.

19.2. Total Suspended Solids Dried at 103-105°C, Method 2540D in Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998.

APPENDIX

BENCHSHEET

Work Order #.: _____ Method: ASTM D 3977-97

Analysis: Sediment in Water

Sample #	Par... Numb...r	...mple Volume ml)	W... Filter + ...ple (1) (g)	Wt. ...ilter + ...sample (...) (g)	Wt. Filter + Dry sample (3) (g)	Wt. Filter (g	Wt. Dry Sa...ple (g)	Sediment (mg/L)	Sediment (mg/L) reported
	1						0.0000	#DIV/0!	#DIV/0!
	2						0.0000	#DIV/0!	#DIV/0!
	3						0.0000	#DIV/0!	#DIV/0!
	4						0.0000	#DIV/0!	#DIV/0!
	5						0.0000	#DIV/0!	#DIV/0!
	6						0.0000	#DIV/0!	#DIV/0!
	7						0.0000	#DIV/0!	#DIV/0!
	8						0.0000	#DIV/0!	#DIV/0!
	9						0.0000	#DIV/0!	#DIV/0!
	10						0.0000	#DIV/0!	#DIV/0!
	11						0.0000	#DIV/0!	#DIV/0!
	12						0.0000	#DIV/0!	#DIV/0!
	13						0.0000	#DIV/0!	#DIV/0!
	14						0.0000	#DIV/0!	#DIV/0!
	15						0.0000	#DIV/0!	#DIV/0!
	16						0.0000	#DIV/0!	#DIV/0!
	17						0.0000	#DIV/0!	#DIV/0!
	18						0.0000	#DIV/0!	#DIV/0!
	19						0.0000	#DIV/0!	#DIV/0!
	20						0.0000	#DIV/0!	#DIV/0!
	21						0.0000	#DIV/0!	#DIV/0!
	22						0.0000	#DIV/0!	#DIV/0!
	23						0.0000	#DIV/0!	#DIV/0!
	24						0.0000	#DIV/0!	#DIV/0!
	25						0.0000	#DIV/0!	#DIV/0!

Calculation: Suspended Solids (mg/L) = Wt. Dry Sa...le (g) ...1000 ...1000 / Volume (ml) Balance#31

APG #:4033 Lot# 220311 ID# TDS/1-32... T.V. = 2... % Rec =

Wt (1)	Start			Wt (2)	Start		Wt (3)	Start		
	Stop				Stop			Stop		
Wt (1)	Start	105		Wt (2)	Start 105		Wt (3)	Start		
Temp	Stop	105		Temp	Stop 105		Temp	Stop	date	time

Analyzed By: Date Analyzed:

Reviewed By: Date Reviewed: